

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**PATENT APPLICATION**

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**COMPOSITIONS OF ANIONIC POLYMERIC  
RHEOLOGY MODIFIERS AND CATIONIC MATERIALS**

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INVENTOR(S)

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### **CROSS REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 60/408,793 filed September 6, 2002, the disclosure of which is hereby incorporated by reference.

### **BACKGROUND OF THE INVENTION**

[0002] Rheology modifiers (thickeners) are generally employed in most personal care products and other products of that nature. Some of the most useful rheology modifiers are anionic polymeric materials that are based on ethylenically unsaturated carboxylic acid monomers which includes crosslinked polyacrylic acid or copolymers of ethylenically unsaturated carboxylic acid monomers and copolymerizable vinyl monomers. Such polymers yield anionic polymeric rheology modifiers that are extremely useful in various personal care products in the cosmetic and toiletry industries.

[0003] In addition to thickeners, such products generally require a variety of other ingredients especially cationic ingredients. Often cationic surfactants, or cationic conditioning agents, are particularly useful. However, cationic surfactants generally are not compatible with anionic polymeric thickening agents. G. Polotti and F. Coda in "Thickener for Cationic Surfactant Solutions" in the Proceedings of the 28th CED Annual Meeting, Barcelona, Spain, 1998, stated: "The thickening of cationic surfactant solutions is often a challenging problem in the detergent industry especially for the formulation of fabric softeners, toilet bowl cleaners, lime scale removers, etc. Part of the problem comes because the most common thickeners, such as those based on cross-linked polyacrylic acid, are anionic species. Although stable and viscous suspensions are achievable, the combination of polyacrylic acid and cationic surfactants forms aggregates that cannot be shared in further dilution. The effect of the cationic species is consequently lost in the strong bond with the anionic ingredients."

[0004] In the Handbook of Cosmetic Science and Technology, First Edition 1993 Elsevier Science Publishers Ltd, on page 17 it is stated:

"Carbomers are incompatible with cationic surfactants and show a significant reduction in viscosity building potential in the presence of electrolytes. For this reason, their use in the stabilization of detergent-based products is very limited."

[0005] Consequently, there is a great need in the above-mentioned products for the ability to employ anionic polymeric thickeners or rheology modifiers such as carbomers in combination with cationic surfactants or other cationic ingredients.

[0006] There are several U.S. patents or published patent applications that disclose the use of rheology modifiers and silicones in various cosmetic or personal care compositions.

[0007] U.S. Patent 4,210,161 discloses a cream rinse composition comprising an anionic polymer and a cationic surfactant capable of forming a water insoluble reaction product. Thus, this patent clearly states that the anionic polymer and a cationic surfactant are incompatible and do form a precipitate but in this formulation, such a precipitate is desirable.

[0008] U.S. Patent 4,710,374 discloses cosmetic compositions containing a cationic polymer and an anionic polymer latex. The patent disclosure clearly stresses that the cationic polymer is of a relatively high molecular weight of between 500 to 3,000,000 but most, if not all, appear to be at least 10,000 molecular weight and more often, about 500,000 molecular weight. Thus, the cationic ingredient is a large molecule with a low charge density. For this reason, the cationic polymer and the anionic polymeric latex are not truly incompatible.

[0009] U.S. Patent 6,071,499 discloses cosmetic compositions with an anionic acrylic polymer and an oxyalkylenated silicone which is nonionic. Since the silicone is not anionic, it cannot complex with a cationic ingredient although it is said to improve the performance of such anionic polymer.

[0010] Published U.S. Application 2003/0108503 A1 discloses a composition comprising a copolymer of methacrylic acid and an alkyl acrylate, a cationic or amphoteric polymer and a functionalized silicone. Apparently, the disclosed anionic polymers are compatible with the disclosed cationic polymeric surfactants. The three components are combined together

without first forming a complex of a cationic polymer with the functionalized silicone. Consequently, no compatibilization or complex formation is involved in the invention disclosed in this published application.

#### **SUMMARY OF THE INVENTION**

[0011] The invention is directed to a method of compatibilizing an anionic polymeric rheology modifier with cationic ingredients, such as a cationic surfactant cationic polymer or a cationic salt, which method comprises complexing a cationic ingredient with an anionic complexing agent before combining the complexed cationic ingredient with an anionic rheology modifier. The invention is further directed to a composition comprising an anionic polymeric rheology modifier and a complexed cationic ingredient and to a personal care or a household composition containing an anionic rheology modifier and a cationic ingredient complexed with an anionic complexing agent.

[0012] When cationic ingredients are combined with anionic polymeric thickeners, because of their incompatibility, usually a precipitate forms, turbidity develops and the thickening effect of the polymers is generally substantially decreased. By first complexing the cationic ingredient(s) with an anionic complexing agent before combining with an anionic polymeric thickener, the incompatible anionic polymer thickeners and the cationic ingredients become compatibilized. When such compatibilized cationic ingredient(s) is combined with an anionic thickener, the viscosity/turbidity profile of the resulting compositions is substantially improved. Thus, the complexing of the cationic materials prior to combining them with a thickener either reduced or eliminated excessive turbidity and the tendency to form precipitates.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0013] FIGS. 1-3 are graphs showing compatibility of Carbopol® ETD 2020 thickener with various complexed cationics when a sufficient complexing agent is used.

[0014] FIGS 4-6 are graphs showing compatibility of various Carbopol® thickeners with various cationics when complexing agents are used.

[0015] FIGS 7-9 show the results of Rubine Dye tests.

[0016] FIGS 10-11 show results of wet comb-through test results when a complex is formed and when the complexing agent is not used.

#### **DETAILED DISCLOSURE**

[0017] The truly unexpected feature of the present invention is the fact that the cationic ingredients, which generally are not compatible with anionic polymeric thickening agents, can be made compatible by complexing them with anionic compatibilizing agents without negatively affecting the performance and function of the cationic ingredients. The cationic ingredients that may be used in personal care products in combination with anionic rheology modifiers are quaternary ammonium salts, polyquaternary ammonium salts, organic or inorganic salts, alkyl amines, amidoamines, ethoxylated amines and alkyl imidazolines which, as such, are incompatible with polymeric anionic rheology modifiers. By "incompatible", is meant that when such cationic ingredients are combined with polymeric anionic rheology modifiers, either a precipitate forms or turbidity develops.

[0018] When cationic ingredients are added to a formulation containing an anionic thickening agent, generally a significant reduction in viscosity results and often a precipitate is formed and turbidity develops. For this reason, the use of anionic thickening agents in combination with cationic ingredients in personal care products and in household products is very limited. This long existing difficulty, however, can be overcome and such materials can be compatibilized by the instant invention, wherein cationic ingredients are first complexed with a compatibilizing agent which is an anionic bulky molecule containing an anionic group such as a sulfate group, sulfonate group, phosphate group, phosphonate or carboxylate groups. By "compatibilized" is meant a substantial reduction of the precipitate or turbidity that would be formed without first complexing the cationic ingredient. By "substantial reduction" is meant a reduction to such a degree that such ingredients (the cationic materials and the anionic thickeners) can be successfully employed in personal care products. Generally such reduction would constitute at least a 50% reduction of turbidity formation and preferably at least 80% reduction such that turbidity of compositions or formulations containing both cationic ingredient(s) and anionic rheology modifier(s) is not greater than 50, often 20 NTU and preferably 15 NTU or less. In clear gels, such as a clear conditioning styling gel, it is preferable that the turbidity be 15 NTU or less and preferably 10 NTU or

less; while in a clear formula shampoo a turbidity of as high as 40 NTU may be acceptable. The level of turbidity that is considered acceptable always depends on the type of product. The use of complexed anionic ingredients of this invention also aid in efficient use of rheology modifiers by often enabling the use of a lesser amount of a thickener yet obtaining desirable properties, thus making the resulting products more cost efficient. There should be practically a complete elimination of precipitate formation.

[0019] Generally the cationic materials are not compatible with the anionic rheology modifiers. However, if the concentration of a cationic material is low enough, they may be compatible. Similarly, if the charge density is low enough (e.g. the charge moiety(s) is dispersed sparsely throughout the molecule) they may also be compatible. Consequently, this invention deals with cationic materials that are incompatible with the specified anionic polymeric rheology modifiers.

#### **Cationic Ingredients**

[0020] Cationic ingredients are commonly used in the personal care industry as surfactants and as conditioning ingredients. Since they are cationic in nature, it allows them to easily deposit onto anionic substrates like hair and skin.

[0021] Quaternary ammonium compounds (i.e. quats) are the most widely used of the many available classes of cationic ingredients which function as conditioning agents. Their outstanding performance characteristics, which greatly contribute to their popularity, are well-known in the industry. Their favorable safety profile, cost-effectiveness and long-term stability are additional factors.

[0022] Quats are used in hair care formulations (e.g. cleansing applications like shampoos, setting and fixing applications like mousses, gels, sprays, spritzes and volume enhancers, and coloring applications like one-part or two-part permanent or semi-permanent dyes) to enhance the shine, combability, appearance, body, slip, feel and general manageability of hair.

[0023] Polyquats are the polymeric counterparts of quats and are used in the same manner as quats, and for the same general purposes. They have additional utility as fixatives

and rheology modifiers, due to their high molecular weight. Their large size also prevents them from penetrating (and thus, irritating) skin, so they enjoy market acceptance in skin care applications as well. In skin care, they are most commonly used as conditioners in personal cleansers like bath gels and body washes.

[0024] Illustrative examples of cationic ingredients are listed below.

A. Polyquaterniums

Hexadimethrine Chloride  
 Hydroxypropyl Guar Hydroxypropyltrimonium Chloride  
 Locust Bean Hydroxypropylthemonium Chloride  
 Polyacrylamidopropyltrimonium Chloride  
 Polymethacrylamidopropyltrimonium Methosulfate  
 Polyquaternium-1\* to 20\*, 22\*, 24\*, 27\* to 37\*, 39\*, 42\* to 50\*

B. Monosubstituted Quaternaries

Hydroxypropyltrimonium Chloride  
 Basic Red 118\*  
 Behenoyl PG-Trimonium Chloride  
 Behentrimonium Chloride  
 Behentrimonium Methosulfate  
 Benzyl Triethyl Ammonium Chloride  
 Bis-Hydroxyethyl Cocomonium Nitrate  
 Bis-Hydroxyethyl Dihydroxypropyl Stearammonium Chloride  
 Bis-Hydroxyethyl Rapeseedmonium Chloride  
 Bis-Hydroxyethyl Tallowmonium Chloride  
 Camphor Benzalkonium Methosulfate  
 Carpronium Chloride  
 Ceteartrimonium Chloride  
 Cetrimonium Bromide, Chloride, Methosulfate, Saccharinate and Tosylate  
 Cetyl Ethyldimonium Ethosulfate  
 Coco-Ethyldimonium Ethosulfate  
 Cocotrimonium Chloride and Methosulfate  
 C4-18 Perfluoralkylethyl Thiohydroxypropyltrimonium Chloride  
 Dextran Hydroxypropyltrimonium Chloride  
 Dimethicone Hydroxypropyl Trimonium Chloride  
 Dodecylbenzyltrimonium Chloride  
 Dodecylhexadecyltrimonium Chloride  
 Dodecylxylylditrimonium Chloride  
 Galactoarabinan Hydroxypropyltrimonium Chloride  
 Ginseng Hydroxypropyltrimonium Chloride  
 Guar Hydroxypropyltrimonium Chloride  
 Hydrogenated Tallowtrimonium Chloride  
 Hydroxypropyl Bistrimonium Diiodide  
 Hydroxypropyltrimonium Honey  
 Hydroxypropyltrimonium Hydrolyzed Whey  
 Isostearyl PG-Trimonium Chloride

B. Monosubstituted Quaternaries (Cont'd)

Isostearyl Ethyldimonium Chloride  
 Lactamidopropyl Trimonium Chloride  
 Lauroyl PG-Trimonium Chloride  
 Laurtrimonium Bromide, Chloride and Trichlorophenoxide  
 Octyldodecyltrimonium Chloride  
 Oleamine Bishydroxypropyltrimonium Chloride  
 Oleoyl PG-Trimonium Chloride  
 Palmitamidopropyltrimonium Chloride  
 Palmitoyl PG-Trimonium Chloride  
 PEG-1 and PEG-10 Coco-Benzonium Chloride  
 PEG-2 and PEG-15 Cocomonium Chloride  
  
 PEG-5 Cocomonium Methosulfate  
 PEG-2 and PEG-15 Oleammonium Chloride  
 PEG-2 and PEG-15 Stearmonium Chloride  
 PEG-5 Stearyl Ammonium Chloride and Lactate  
 PEG-20 Tallow Ammonium Ethosulfate  
 PEG-5 Tallow Benzonium Chloride  
 PPG-9, PPG-25 and PPG-40 Diethylmonium Chloride  
 Quaternium-16\*, 22\*, 26\*, 30\*, 33\*, 52\*, 60\*, 61\*, 75\* and 88\*  
 Soytrimonium Chloride  
 Stearoyl PG-Trimonium Chloride  
 Steartrimonium Bromide  
 Steartrimonium Methosulfate  
 Steartrimonium Sacchannate  
 Tallow Trihydroxyethylammonium Acetate  
 Tallowtrimonium Chloride

C. Disubstituted Quaternaries

Behenalkonium Chloride  
 Benzalkonium Bromide and Chloride  
 Benthethonium Bromide or Chloride  
 Benzalkonium Cetyl Phosphate  
 Benzoxonium Chloride  
 C12-18 Dialkyldemonium Chloride  
 Cetalkonium Chloride  
 Cetearalkonium Bromide  
 Cetethyldimonium Bromide  
 Cetethyl Morpholinium Ethosulfate  
 Cetyl Pyrrolidonylmethyl Dimonium Chloride  
 Cocoalkonium Chloride  
 Denatonium Benzoate and Saccharide  
 Dibehenyl/Diarachidyl Dimonium Chloride  
 Dibehenyldimonium Chloride and Methosulfate  
 Di-C12-15, C12-18 and C14-18 Alkyl Dimonium Chloride  
 Dicytyldimonium Chloride  
 Dicocodimonium Chloride  
 Dicoylethyl Hydroxyethylmonium Methosulfate  
 Didecyldimonium Chloride



C. Disubstituted Quaternaries (Cont'd)

Dihydrogenated Palmolethyl Hydroxyethylmonium Methosulfate  
 Dihydrogenated Palmoyl Hydroxyethylmonium Methosulfate  
 Dihydrogenated Tallow Benzylmonium Chloride and Hectorite  
 Dihydrogenated Tallowethyl Hydroxyethylmonium Methosulfate  
 Dihydrogenated Tallow Hydroxyethylmonium Methosulfate  
 Dihydrogenated Tallow Hydroxyethylmonium Methosulfate

Dihydrogenated Tallowayethyl Hydroxyethylmonium Methosulfate  
 Dihydroxypropyl PEG-5 Linoleammonium Chloride  
 Diisostearamidopropyl Epoxypropylmonium Chloride  
 Dilaureth-4 Dimonium Chloride  
 Dilauryl Acetyl Dimonium Chloride  
 Dilauryldimonium Chloride  
 Dimethyl PABA Ethyl Cetearyldimonium Tosylate  
 Dimethyl PABA Midopropyl Laurdimonium Tosylate  
 Dioleoylamidoethyl Hydroxyethylmonium Methosulfate  
 Dioleoyl Edetolmonium Methosulfate  
 Dioleoyl EDTHP Monium Methosulfate  
 Dipalmitoylethyl Dimonium Chloride  
 Dipalmitoylethyl Hydroxyethylmonium Methosulfate  
 Dipalmoylethyl Hydroxyethylmonium Methosulfate  
 Dipalmoylisopropyl Dimonium Methosulfate  
 Disoydimonium Chloride  
 Disoyolethyl Hydroxyethylmonium Methosulfate  
 Disteardimonium Hectorite  
 Distearth-6 Dimonium Chloride  
 Distearoylethyl Dimonium Chloride  
 Distearoylethyl Hydroxyethylmonium Methosulfate  
 Distearoylpropyl Trimonium Chloride  
 Distearlydimonium Chloride  
 Distearyl Epoxypropylmonium Chloride  
 Ditallowamidoethyl Hydroxypropylmonium Methosulfate  
 Ditallow Dimonium Cellulose Sulfate  
 Ditallowdimonium Chloride  
 Ditallowoylethyl Hydroxyethylmonium Methosulfate  
 Ditridecyldimonium Chloride  
 Domiphen Bromide  
 Erucalkonium Chloride  
 Hydrogenated Tallowalkonium Chloride  
 Hydroxycetyl Hydroxyethyl Dimonium Chloride  
 Hydroxyethyl Cetyldimonium Chloride and Phosphate  
 Hydroxyethyl Laurdimonium Chloride  
 Hydroxyethyl Tallowdimonium Chloride  
 Hydroxypropyl Biscetearyldimonium Chloride  
 Hydroxypropyl Bisolelydimonium Chloride  
 Hydroxypropyl Bisstearyldimonium Chloride  
 Isostearyl Laurdimonium Chloride  
 Lauralkonium Bromide and Chloride  
 Lauryl Methyl Gluceth-10 Hydroxypropyldimonium Chloride

C. Disubstituted Quaternaries (Cont'd)

Methylbenzethonium Chloride  
 Myristaklonium Chloride, Bromide and Saccharinate  
 Olealkonium Chloride  
 Oleoyl Epoxypropyldimonium Chloride  
 Panthenyl Hydroxypropyl Steardimonium Chloride  
 PEG-9 and 25 Diethylmonium Chloride  
 PEG-2 Dimeadowfoamamidoethylmonium Methosulfate  
 PEG-3 Dioleoylamidoethylmonium Methosulfate  
 PEG-5 Ditridecylmonium Chloride  
 PEG-8 Palmitoyl Methyl Diethonium Methosulfate  
 PEG-10 Stearyl Benzonium Chloride  
 PEG-3 Tallow Propylenedimonium Dimethosulfate  
 Quaternium-8\*, 14\*, 18\*, 24\*, 43\*, 53\*, 63\*, 70\*, 71\* and 84\*  
 Quaternium-18 Bentonite\*  
 Quaternium-18 Benzalkonium Bentonite  
 Quaternium-18 Hectorite\* and Methosulfate\*  
 Sodium Coco PG-Dimonium Chloride Phosphate  
 Soy Dihydroxypropyldimonium Glucoside  
 Soydimonium Hydroxypropyl Hydrolyzed Wheat Protein  
 Soyethylidimonium Ethosulfate  
 Stearalkonium Bentonite, Chloride and Hectorite  
 Stearyl Ethylhexyldimonium Chloride and Methosulfate  
 Stearyl PG-Dimonium Chloride Phosphate  
 Tallowalkonium Chloride  
 Tallowdimonium Propyltrimonium Dichloride  
 Thiamine Diphosphate

D. Tetrasubstituted Quaternaries

Quaternium-15\*  
 Tetrabutyl Ammonium Bromide  
 Tetramethylammonium Chloride

E. Heterocyclic Quaternaries

Cetylpyridinium Chloride  
 Cocoyl Benzyl Hydroxyethyl Imidazolinium Chloride  
 Cocoyl Hydroxyethylimidazolinium PG-Chloride Phosphate  
 Dequalnum Acetate and Chloride  
 Dimethylaminostyrol Heptyl Methyl Thiazolium Iodide  
 Hydroxyanthraquinoneaminopropyl Methyl Morpholinium Methosulfate  
 Isostearyl Benzylimidonium Chloride  
 Isostearyl Ethylimidazolinium Ethosulfate  
 Lapyrium Chloride  
 Lauryl Isoquinolinium Bromide and Saccharinate  
 Laurylpyridinium Chloride  
 Platonin\*  
 Quaternium-27\*, 45\*, 51\*, 56\*, 72\*, 73\*, 83\* and 87\*  
 Soyethyl Morpholinium Ethosulfate  
 Stearyl Hydroxyethylimidonium Chloride  
 Tall Oil Benzyl Hydroxyethyl Imidazolinium Chloride

F. Substituted Amido Quaternaries

Acetamidoethoxybutyl Trimonium Chloride  
 Acetamidopropyl Trimonium Chloride  
 Acrylamedopropyltrimonium Chloride/Acrylamide Copolymer  
 Acrylamidopropyltrimonium Chloride/Acrylates Copolymer  
 Almondamidopropalkonium Chloride  
 Apricotamidopropyl Ethyldimonium Ethosulfate  
 Avocadamidopropalkonium Chloride  
 Babassuamidopropalkonium Chloride  
 Behenamidopropyl Ethyldemonium Ethosulfate  
 Behenamidopropyl PG-Dimonium Chloride  
 Canolamidopropyl Ethyldimonium Ethosulfate  
 Carboxymethyl Isostearamidopropyl Morpholine  
 Cinnamidopropyltrimonium Chloride  
 C14-20 and C18-22 Isoalkylamidopropylethyldimonium Ethosulfate  
 Cocamidopropyl Betaine MEA Chloride  
 Cocamidopropyldimonium Hydroxypropyl Hydrolyzed Collagen  
 Cocamidopropyl Ethyldimonium Ethosulfate  
 Cocamidopropyl PG-Dimonium Chloride and Chloride Phosphate  
 Cocamidopropyltrimonium Chloride  
 Dihydrogenated tallowamidoethyl Hydroxyethylmonium Chloride  
 and Methosulfate  
 Hydroxypropyl Bisisostearamidopropyldimonium Chloride  
 Hydroxystearamidopropyl Trimonium Chloride  
 Hydroxystearamedopropyl Trimonium Methosulfate  
 Isononamidopropyl Ethyldimonium Ethosulfate  
 Isostearamidopropyl Epoxypropyl Dimonium Chloride  
 Isostearamidopropyl Epoxypropylmorpholinium Chloride  
 Isostearamidopropyl Ethyldimonium Ethosulfate  
 Isostearamidopropyl Ethylmorpholinium Ethosulfate  
 Isostearamidopropyl Laurylaceto-dimonium Chloride  
 Isostearamidopropyl PG-Dimonium Chloride  
 Isostearamenopropalkonium Chloride  
 Isostearyl Behenamidopropyl Betainate  
 Isostearyl Dilinoleamidopropyl Betainate  
 Isostearyl Racinoleamidopropyl Betainate  
 Methylene bis (tallowacetamididmonium Chloride)  
 Lauramidopropyl Acetamidodimonium Chloride  
 Lauramidopropyl PG-Dimonium Chloride  
 Linoleamidopropyl Ethyldimonium Ethosulfate  
 Linoleamidopropyl PG-Dimonium Chloride Phosphate and  
 Phosphate Dimethicone  
 Minkamidopropalkonium Chloride  
 Minkamidopropyl Ethyldimonium Ethosulfate  
 Oleamidopropyldimonium Hydroxypropyl Hydrolyzed Collagen  
 Oleamidopropyl Ethyldimonium Ethosulfate  
 Oleamidopropyl PG-Dimonium Chloride  
 Rapeseedamidopropyl Benzyldimonium Chloride  
 Rapeseedamidopropyl Epoxypropyl Dimonium Chloride

- F. Substituted Amido Quaternaries (Con'd)  
 Rapeseedamidopropyl Ethyldimonium Ethosulfate  
 Ricebranamidopropyl Hydroxyethyl Dimonium Chloride  
 Ricinoleamidopropyl Ethyldimonium Ethosulfate  
 Ricinoleamidopropyltrimonium Chloride and Methosulfate  
 Saffloweramidopropyl Ethyldimonium Ethosulfate  
 Sodium Borageamidopropyl PG-Dimonium Chloride Phosphate  
 Sodium Emuamidopropyl PG-Dimonium Chloride Phosphate  
 Sodium Milkamidopropyl PG-Dimonium Chloride Phosphate  
 Sodium Oleamidopropyl PG-Dimonium Chloride Phosphate  
 Sodium Sunfloweramidopropyl PG-Dimonium Chloride Phosphate  
 Soyamidoethyltrimonium Hydroxypropyl Hydrolyzed Wheat Protein  
 Soyamidopropalkonium Chloride  
 Soyamidopropyl Ethyldimonium Ethosulfate  
 Stearamidopropalkonium Chloride  
 Stearamidopropyl Cetearyl Dimonium Tosylate  
 Stearamidopropyl Ethyldimonium Ethosulfate  
 Stearamidopropyl PG-Dimonium Chloride Phosphate  
 Stearamidopropyl Pyrrolidonylmethyl Dimonium Chloride  
 Stearamidopropyl Trimonium Methosulfate  
 Undecylenamidopropyltrimonium Methosulfate  
 Wheat Germamidopropalkonium Chloride  
 Wheat Germamidopropalkonium Hydroxypropyl Hydrolyzed Wheat Protein  
 Wheat Germamidopropyl Epoxypropyldimonium Chloride  
 Wheat Germamidopropyl Ethyldimonium Ethosulfate
- G. Quaternized Keratin  
 AMP-Isostearoyl Gelatin/Keratin Amino Acids/Lysine  
 Cocodimonium Hydroxypropyl Hydrolyzed Hair Keratin and Keratin  
 Hydroxypropyltrimonium Gelatin and Hydrolyzed Keratin  
 Lauryldimonium Hydroxypropyl Hydrolyzed Keratin  
 Quaternium-79 Hydrolyzed Keratin\*  
 Steardimonium Hydroxypropyl Hydrolyzed Keratin
- H. Quaternized Collagen  
 Benzyltrimonium Hydrolyzed Collagen  
 Cocodimonium Hydroxypropyl Hydrolyzed Collagen  
 Hydroxypropyltrimonium Hydrolyzed Collagen  
 Lauryldimonium Hydroxypropyl Hydrolyzed Collagen  
 Propyltrimonium Hydrolyzed Collagen  
 Quaternium-76 and 79 Hydrolyzed Collagen\*  
 Steardimonium Hydroxypropyl Hydrolyzed Collagen  
 Steartrimonium Hydroxyethyl Hydrolyzed Collagen  
 Triethonium Hydrolyzed Collagen Ethosulfate
- I. Quaternized Amino Acids  
 Cocodimonium Hydroxypropyl Silk Amino Acids  
 Gelatin/Keratin Amino Acids/Lysine Hydroxypropyltrimonium Chloride

J. Quaternized Proteins

Cocodimonium Hydroxypropyl Hydrolyzed Casein, Silk, Rice Protein,  
Soy Protein & Wheat Protein  
Gelatin/Lysine/Polyacrylamide Hydroxypropyltrimonium Chloride  
Hydroxypropyltrimonium Hydrolyzed Casein and Conchiolin Protein  
Hydroxypropyltrimonium Hydrolyzed Rice Bran Protein, Silk, Vegetable  
Protein,  
Wheat Protein, Wheat Protein/Siloxysilicate  
Laurdimonium Hydroxypropyl Hydrolyzed Soy Protein and Wheat Protein/  
Siloxysilicate  
Lauryldimonium Hydroxypropyl Hydrolyzed Casein, Silk and Soy Protein  
Propyltrimonium Hydrolyzed Soy Protein and Wheat Protein  
Quaternium-79 Hydrolyzed Milk Protein\*, Silk\*, Soy Protein\*  
and Wheat Protein\*  
Quaternium-86\*  
Steardimonium Hydroxypropyl Hydrolyzed Casein, Rice Protein, Silk,  
Soy Protein and Vegetable Protein  
Steardimonium Hydroxypropyl Wheat Protein

K. Salts of Divalent or Polyvalent Cations

Aluminum Acetate and Acetate Solution  
Aluminum Benzoate, Butoxide, Citrate, Diacetate, Dicyetyl Phosphate, Lactate,  
Methionate, PCA, Sucrose Octasulfate and Triformate  
Aluminum/Magnesium Hydroxide Stearate  
Antimony Potassium Tartrate  
Barium Gluconate  
Bismuth Citrate and Subgallate  
Brucine Sulfate  
Calcium Acetate, Ascorbate, Benzoate, Citrate, Cyclamate, DNA,  
Fructoheptonate, Glucoheptonate, Gluconate, Glycerophosphate, Lactate,  
Pantetheine Sulfonate, Pantothenate, Paraben, Propionate, Saccharine,  
Salicylate, Sorbate, Stearoyl Lactylate, Tartarate and Thioglycolate  
Calcium Disodium EDTA  
Cobalt Gluconate  
CopperDNA, Gluconate, PCA, PCA Methylsilanol, Picolinate and Usnate  
Cupric Acetate  
Feric Ammonium Citrate  
Ferric Citrate and Glycerophosphate  
Ferrous Aspartate, Aglucoheptonate and Gluconate  
Iron Picolinate  
Isopropyl Titanium Triisostearate  
Lead Acetate  
Magnesium Acetate, Ascorbate, Ascorbate/PCA, Ascorbyl Phosphate,  
Benzoate, Citrate, DNA, Glucoheptonate, Gluconate, Glycerophosphate, PCA,  
Propionate, Salicylate and Thioglycolate  
Magnesium Laureth-11 Carboxylate  
Manganese Gluconate  
Manganese Glycerophosphate  
Manganese PCA  
Molybdenum Aspartate

- K. Salts of Divalent or Polyvalent Cations (Cont'd)  
 Nickel Gluconate  
 Phenyl Mercuric Acetate, Benzoate, Borate and Chloride  
 Strontium Acetate  
 Strontium Thioglycolate  
 Zinc Acetate, Citrate, Cysteinate, Dibutyldithiocarbamate, Glucoheptonate,  
 Gluconate, Glycyrrhelinic Acid, Lactate, Picolinate and Pyrithione  
 Zinc Formaldehyde Sulfoxylate  
 Zinc PCA
- L. Pigments  
 Zinc Oxide, Iron Oxides, Titanium Dioxide
- M. Organic Amines  
 Alanine Glutamate  
 Allantoin Acetyl Methionine, Ascorbate, Biotin, Calcium Pantothenate,  
 Galacturonic Acid, Glycyrrhethinic Acid, PABA and Polygalacturonic Acid  
 Amodimethicone Hydroxystearate  
 Arginine Aspartate, DNA and PCA  
 Arginine Glutamate  
 Arginine Hexyldecyl Phosphate  
 Chitosan Adipate, Ascorbate, Glycolate and Salicylate  
 Chloramine T  
 Chlorhexidine Diacetate, Digluconate and Dihydrochloride  
 Chlorophyllin-Copper Complex  
 Ciclopirox Olamine  
 Cysteamine HCl  
 Cysteine DNA  
 DEA-Cetyl Phosphate  
 DEA-Hydrolyzed Lecithin  
 DEA-Methoxycinnamate  
 Dibehenamidopropyl dimethylamine Dilinoleate  
 Dibromopropamide Diisethionate  
 Diglycol Guanidine Succinate  
 Dihydroxyethyl Tallowamine Oleate  
 Dilithium Oxalate  
 Dimethicone Propylene diamine Behenate  
 Ethanolamine Dithiodiglycolate, Glycerophosphate and Thioglycolate  
 Ethyl Hydroxy Picolinium Lactate  
 Ethyl Lauroyl Arginate HCl  
 Guanidine Carbonate, HCl and Phosphate  
 Hexamidine Diisethionate and Paraben  
 Isostearamidopropyl Dimethylamine Gluconate, Glycolate and Lactate  
 Isostearamidopropyl Morpholine Lactate  
 Lauryl Isoquinolinium Saccharinate  
 Lauryl PCA  
 Lysine DNA and Glutamate  
 MEA-Benzoate, Dicetearyl Phosphate, o-Phenylphenate, Salicylate,  
 Thiolactate and Undecylenate  
 MEA-Laureth-6 Carboxylate

- M. Organic Amines (Cont'd)  
MEA PPG-6 Laureth-7 Carboxylate  
MEA PPG-8 Steareth-7 Carboxylate  
Methyl Hydroxycetyl Glucaminium Lactate  
Methylsilanol Hydroxyproline Aspartate  
Nicotinyl Tartrate  
Olivamidopropyl Dimethylamine Lactate  
Oxyquinoline Benzoate and Sulfate  
PCA Ethyl Cocoyl Arginate  
Piroctone Olamine  
Pyridoxine HCl  
Saccharated Lime  
TEA-Cocoyl Alaninate  
TEA-EDTA  
TEA-Lauroyl Lactylate  
TEA-Phenylbenzimidazole Sulfonate  
Thurfylnicotinate HCl
- N. Organic Imidazolines  
Stearyl Hydroxyethyl Imidazoline
- O. Ethoxylated Amines  
PEG-15 Tallowamine  
PEG-cocopolyamine
- P. Quaternized Cellulose  
PG-Hydroxyethylcellulose Cocodimonium Chloride  
PG-Hydroxyethylcellulose Lauryldimonium Chloride  
PG-Hydroxyethylcellulose Stearyldimonium Chloride
- Q. Quaternized Silicone  
Quaternium-80\*  
Silicone Quaternium-1\* to 13\*
- R. Multifunctional Quaternaries  
Quaternium-77\*, 78\*, 81\*, 82\* and 85\*
- S. Tertiary Substituted Quaternaries  
Tricetylmonium Chloride

\*The composition of this material is identified in the International Cosmetic Ingredients Dictionary and Handbook, 8th ed. (2000), the Cosmetic Toiletry and Fragrance Association, 1101 17th St., NW, Suite 300, Washington, D.C. 20036-4702.

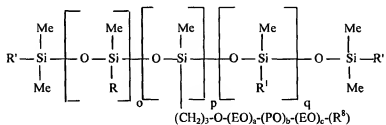
#### **Compatibilizing Agents**

[0025] The compatibilizing agents or complexing agents which complex with the cationic ingredients may be any material that contains a "bulky" molecule having an anionic group.

The "bulky" molecule should not be reactive chemically with either the anionic thickening agent or the cationic ingredients. The "bulky" molecule will generally have a molecular weight of at least 500 Mn, preferably at least 1,000 Mn, and may have a molecular weight of up to 50,000 Mn, but generally up to 25,000 Mn. Usually the "bulky" molecule is a polymeric material having at least three repeat units. The composition of the polymeric materials may be heterogeneous and predominantly may be polysilicones, acrylic copolymers, polyalkylene glycol such as polyethylene glycol and polypropylene glycol, polyvinyl alcohol, polyvinyl acetate, polysaccharide such as starch and cellulose or polyurethane. Polyalkylene glycols may contain terminal groups such as, but not limited, allyl, propenyl, propyl and hydrogen or others. These polymeric or "bulky" groups must contain anionic groups which will complex with the cationic ingredients. The preferred anionic groups are carboxylate ( $-\text{COOH}$ ), sulfonate ( $-\text{SO}_3\text{H}$ ), sulfate ( $-\text{OSO}_3\text{H}$ ), phosphate ( $-\text{OP}(\text{OH})_2$ ) and phosphonate ( $-\text{PO}(\text{OH})_2$ ). The anionic groups complex with the cationic ingredients preventing the cationic ingredients from interfering with the anionic thickening agent and permitting the thickening agent to perform its viscosity building function. Although, in principle, any polymeric material containing anionic groups may be employed, it is preferable to employ silicones because they also serve to condition keratinous substances such as hair in shampoos, hair rinses, hair gels and hair dyes; or skin in lotions, creams and hand sanitizers; or nails in nail strengtheners or coatings and cuticle softeners; or lips in lipsticks, lip balms and the like.

[0026] The preferred silicone complexing agents may be represented generically

(1)



wherein:

Me is methyl;

R and R' are independently selected from methyl,  $-\text{OH}$ ,  $-\text{R}^7$ , and  $-\text{R}^9-\text{A}$  or  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_x-(\text{PO})_y-(\text{EO})_z-\text{G}$  with the proviso that both R and R' are not methyl,  $-\text{OH}$  or  $\text{R}^7$ ;



$R^1$  is selected from lower alkyl  $\text{CH}_3(\text{CH}_2)_n-$  or phenyl where  $n$  is an integer from 0 to 22;

$a$ ,  $b$ , and  $c$  are integers independently ranging from 0 to 100;

EO is  $-(\text{CH}_2\text{CH}_2\text{O})-$ ;

PO is  $-\overset{\text{CH}_3}{\underset{|}{\text{CH}_2\text{CHO}}}-$ ;

$o$  is an integer ranging from 1 to 200;

$q$  is an integer ranging from 0 to 1000;

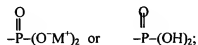
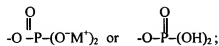
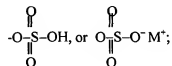
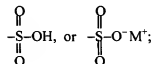
$p$  is an integer ranging from 0 to 200;

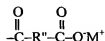
$R^7$  is aryl, alkyl, aralkyl, alkaryl, or alkenyl group of 1-40 carbons;

$R^8$  is hydrogen or  $R^7$  or  $\text{C}(\text{O})-\text{X}$  wherein  $\text{X}$  is aryl, alkyl, aralkyl, alkaryl, alkenyl group of 1-40 carbons, or a mixture thereof;

$R^9$  is divalent group selected from alkylene of 1-40 carbons which may be interrupted with arylene group of 6 to 18 carbons or an alkylene group containing unsaturation of 2 to 8 carbons;

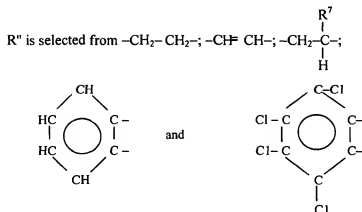
$A$  and  $G$  are independently are selected from





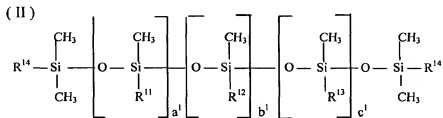
where

R'' is a divalent group selected from alkylene of 1-40 carbons which may be interrupted with an arylene group of 6 to 18 carbons or an alkylene group of 2 to 8 carbons, and is preferably selected from the



where M is Na, K, Li,  $\text{NH}_4$ ; or an amine containing alkyl, aryl, akenyl, hydroxyalkyl, arylalkyl or alkaryl groups.

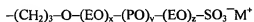
[0027] Another category of silicone complexing agents is silicone sulfates which may be represented by the following formula:



wherein

R<sup>11</sup> is selected from lower alkyl having one to eight carbon atoms or phenyl,

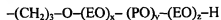
R<sup>12</sup> is



M is a cation and is selected from Na, K, Li, or  $\text{NH}_4$ ;

x, y and z are integers independently ranging from 0 to 100;

$\text{R}^{13}$  is



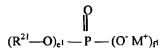
$\text{R}^{14}$  is methyl or hydroxyl;

$a^1$  and  $c^1$  are independently integers ranging from 0 to 50;

$b^1$  is an integer ranging from 1 to 50;

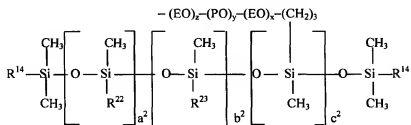
A still further category of silicone complexing agents may be represented as follows:

( III )



wherein

$\text{R}^{21}$  is



$a^2$  is an integer from 0 to 200;

$b^2$  is an integer from 0 to 200;

$c^2$  is an integer from 1 to 200;

$\text{R}^{14}$  is as defined above;

$\text{R}^{22}$  is selected from  $-(\text{CH}_2)_6\text{CH}_3$  and phenyl;

n is an integer from 0 to 10;

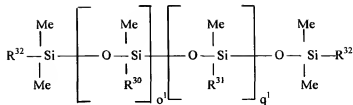
$\text{R}^{23}$  is  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_{x1}-(\text{PO})_{y1}-(\text{EO})_{z1}-\text{H}$ ;

$x^1$ ,  $y^1$  and  $z^1$  are integers and are independently selected from 0 to 20;

$e^1$  and  $f^1$  are 1 or 2 with the proviso that  $e+f=3$ ;

M is selected from H, Na, K, Li, or  $\text{NH}_4$ ; and

( IV )



wherein;

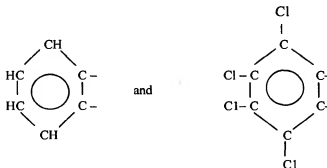
Me is methyl;

R<sup>30</sup> and R<sup>32</sup> independently are CH<sub>3</sub> or

-(CH<sub>2</sub>)<sub>3</sub>-O-(EO)<sub>a</sub>-(PO)<sub>b</sub>-(EO)<sub>c</sub>-C(O)-R<sup>33</sup>-C(O)-OH;

with the proviso that both R<sup>30</sup> and R<sup>32</sup> are not -CH<sub>3</sub>;

R<sup>33</sup> is selected from -CH<sub>2</sub>-CH<sub>2</sub>-; -CH=CH-; -CH<sub>2</sub>-C(R<sup>37</sup>)-H;



R<sup>37</sup> is alkyl having from 1 to 22 carbon atoms;

R<sup>31</sup> is selected from lower alkyl (having 1-4 carbons), CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub><sup>1</sup>- and phenyl;

n<sup>1</sup> is an integer from 0 to 8;

a<sup>3</sup>, b<sup>3</sup> and c<sup>3</sup> are integers independently ranging from 0 to 20;

EO is an ethylene oxide residue -(CH<sub>2</sub>CH<sub>2</sub>-O)-;

PO is a propylene oxide residue -(CH<sub>2</sub>CH(CH<sub>3</sub>)-O)-;

o<sup>1</sup> is an integer ranging from 1 to 200;

q<sup>1</sup> is an integer ranging from 0 to 500.

It should be noted that in the above structure units EO and PO may be in random and block structures.

**[0028]** Such silicone carboxylates are disclosed in greater detail in U.S. Patent 5,296,625, the disclosure of which is incorporated herein by reference. Still further silicone complexing agents are silicones containing a multiplicity of different anionic substituents. Such silicones

can be prepared by reacting two or more types of anionic silicones already disclosed using reactions well known to those in the art. The resulting molecule could be a hybrid of the starting silicones and would, therefore, contain multiple types of anionic functional groups. The properties of the silicone can be optimized in such a fashion. One type of reaction, the silicone equilibration reaction, involves charging a reactor with raw materials, adding a suitable catalyst, mixing with heat, and then neutralizing the catalyst. The Chemistry is discussed in *Silicone in Organic, Organometallic and Polymer Chemistry* (Michael Brook) – John Wiley and Sons, New York, 2000, pp. 261-266.

[0029] The amount of the anionic complexing agent required to complex the cationic ingredients will depend on the specific cationic ingredients (the quat, polyquat, organic salt, etc.), the amount of the cationic ingredients present and the overall pH of the final formulation. The lower the pH of the final formulation, the greater the amount of the complexing agent is required. In view of the above-mentioned variables, it will be necessary to conduct some routine testing to arrive at the optimum amount of the anionic complexing agent, such as a silicone, to be used in a particular formulation to provide the desired results. Generally, the weight ratio of the anionic complexing agent, such as the anionic silicone complexing agent, to the cationic ingredient or ingredients, will be in the range of 0.1-10 to 1. Preferably, the weight ratio of the complexing agent to the cationic ingredient(s) will be 0.5-6 to 1 and most preferably 1.5-3 to 1.

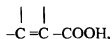
#### **Anionic Polymeric Rheology Modifiers**

[0030] The polymeric rheology modifiers (thickening agents) that normally are not compatible with cationic ingredients, may be used in various formulations in combination with complexed cationic ingredients. Therefore, anionic polymeric rheology modifiers may be employed in the compositions of this invention.

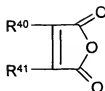
[0031] Generally such anionic polymeric rheology modifiers are either homopolymers obtained from ethylenically unsaturated monomers containing carboxylic groups or ethylenically unsaturated monomers derived from those that contain carboxylic groups, such as acid hydrides, anhydrides or esters. These include the homopolymers of such carboxylic group containing monomers or ethylenically unsaturated anhydrides or copolymers containing at least 1% by weight of such carboxylic monomers or anhydride monomers,

preferably at least 5% and more preferably at least 10%. Prior art discloses a variety of such homopolymers and copolymers that are useful as thickening agents. Illustrative examples of such thickening agents are discussed below.

[0032] The carboxylic monomers useful in the production of thickener polymers are the olefinically-unsaturated carboxylic acids containing at least one activated carbon-to-carbon olefinic double bond, and at least one carboxyl group, that is, an acid containing an olefinic double bond which readily functions in polymerization because of its presence in the monomer molecule either in the alpha-beta position with respect to a carboxyl group thusly,

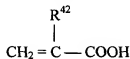


or as a part of a terminal methylene grouping thusly,  $CH_2=C<$ . In the alpha-beta acids the close proximity of the strongly polar carboxyl group to the double-bonded carbon atoms has a strong activating influence rendering the substances containing this structure very readily polymerizable. The presence of a terminal methylene grouping in a carboxylic monomer makes this type of compound much more easily polymerizable than if the double bond were intermediate in the carbon structure. Olefinically-unsaturated acids of this class include such widely divergent materials as the acrylic acids typified by acrylic acid itself, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, alpha-cyano acrylic acid, beta methyl-acrylic acid (crotonic acid), alpha-phenyl acrylic acid, beta-acryloxy propionic acid, sorbic acid, alpha-chloro sorbic acid, angelic acid, cinnamic acid, p-chloro cinnamic acid, beta-styryl acrylic acid (1-carboxy-4-phenyl butadiene-1,3), itaconic acid, citraconic acid, messaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, and tricarboxy ethylene. As used herein, the term "carboxylic acid" includes the polycarboxylic acids and those acid anhydrides, such as maleic anhydride, wherein the anhydride group is formed by the elimination of one molecule of water from two carboxyl groups located on the same polycarboxylic acid molecule. Anhydrides of the types formed by elimination of water from two or more molecules of the same or different unsaturated acids, such as acrylic anhydride, are not included because of the strong tendency of their polymers to hydrolyze in water and alkali. Maleic anhydride and the other acid anhydrides useful herein have the general structure



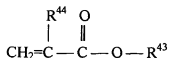
wherein  $R^{40}$  and  $R^{41}$  are independently selected from the group consisting of hydrogen, cyanogens ( $-C \equiv N$ ), hydroxyl, lactam and lactone groups and alkyl, aryl, alkaryl, aralkyl, and cycloalkyl groups such as methyl, ethyl, propyl, octyl, decyl, phenyl, tolyl, xylyl, benzyl, cyclohexyl and the like.

[0033] The preferred carboxylic monomers for use in this invention are the monoolefinic acrylic acids having the general structure



wherein  $R^{42}$  is a substituent selected from the class consisting of hydrogen, halogen, hydroxyl, lactone, lactam cyanogen ( $-CN$ ), monovalent alkyl group (1 to 4 carbons), monovalent aryl group (6 to 12 carbons), monovalent aralkyl group (7 to 12 carbons), monovalent alkaryl group (7 to 12 carbons) and monovalent cycloaliphatic group (4 to 8 carbons). Of this class, acrylic acid itself is most preferred because of its generally lower cost, ready availability, and ability to form superior polymers. Another particularly preferred carboxylic monomer is maleic anhydride.

[0034] The preferred acrylic ester monomers having long chain aliphatic groups are derivatives of acrylic acid represented by the formula:



wherein  $R^{43}$  is hydrogen or an alkyl group having from 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms and  $R^{44}$  is hydrogen or a methyl group. Representative higher alkyl acrylic esters are decyl acrylate, lauryl acrylate, stearyl acrylate, behenyl acrylate and melissyl acrylate and the corresponding methacrylates. Mixtures of two or three or more long chain acrylic esters may be successfully polymerized with one of the carboxylic monomers to provide useful thickening resins of this invention.

[0035] The preferred crosslinking monomer, if one is employed, is a polyalkenyl polyether having more than one alkenyl ether grouping per molecule. The most useful possess alkenyl groups in which an olefinic double bond is present attached to a terminal methylene grouping,  $\text{CH}_2=\text{C}<$ . They are made by the etherification of a polyhydric alcohol containing at least 4 carbon atoms and at least 3 hydroxyl groups. Compounds of this class may be produced by reacting an alkenyl halide, such as allyl chloride or allyl bromide with a strongly alkaline aqueous solution of one or more polyhydric alcohols. The product is a complex mixture of polyethers with varying numbers of ether groups. Analysis reveals only the average number of ether groupings on each molecule. Efficiency of the polyether crosslinking agent increases with the number of potentially polymerizable groups on the molecule. It is preferred to utilize polyethers containing an average of two or more alkenyl ether groupings per molecule. Other crosslinking monomers include for example, diallyl esters, dimethallyl ethers, allyl or menthallyl acrylates and acrylamides, tetraallyl tin, tetravinyl silane, polyalkenyl methanes, diacrylates and dimethacrylates, divinyl compounds, polyallyl phosphate, diallyloxy compounds and phosphite esters and the like.

[0036] Monomeric mixtures of the carboxylic monomer and the long chain acrylic ester monomer preferably contain 95 to 50 weight percent carboxylic monomer and 5 to 50 weight percent acrylic ester monomer.

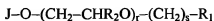
[0037] The above-discussed polymeric thickening agents are disclosed in greater detail in U.S. Patent 3,940,351, the disclosure of which is incorporated herein by reference. Related polymeric thickeners are disclosed in U.S. Patent 3,915,921, the disclosure of which is also incorporated herein by reference.

[0038] Another class of thickeners is represented by crosslinked copolymers obtainable by copolymerization of a monomeric system comprising:

- a) from about 10 to about 97% by weight of at least one ethylenically unsaturated mono- or dicarboxylic acid;
- b) from 0 to about 80% by weight of at least one ( $\text{C}_{1-30}$ ) alkyl or aralkyl ester of an ethylenically unsaturated mono- or dicarboxylic acid;



c) from about 0.5 to about 80% by weight of at least one associative monomer which is an ester of formula



wherein

J is an ethylenically unsaturated acyclic residue, optionally containing an additional carboxylic group, wherein, optionally, said additional carboxylic group may be esterified with a (C<sub>1</sub>.C<sub>20</sub>) aliphatic alkyl group;

R<sub>1</sub> is an alkyl, alkylphenyl or aralkyl residue having from 1 to 30 carbon atoms;

R<sub>2</sub> is hydrogen, methyl or ethyl;

r is comprised between 0 and 50;

s is comprised between 0 and 30;

d) from 0 to about 20% by weight of at least one ethylenically unsaturated amide;

e) from about 0.2 to about 20% by weight of at least one diester between a polyoxyalkyleneglycol or an emulsifier having at least two free OH-groups and an ethylenically unsaturated carboxylic acid, as the cross-linking agent;

f) from 0 to about 20% by weight of at least one ethylenically unsaturated sulfonic acid.

**[0039]** Examples of ethylenically unsaturated mono- or dicarboxylic acids as indicated under a) are, for example, acrylic, methacrylic, itaconic, maleic, sorbic, crotonic acids, and analogs. Among these, acrylic and methacrylic acids are the preferred ones.

**[0040]** Preferred esters of ethylenically unsaturated mono- or dicarboxylic acids indicated under b) are methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, ethyl methacrylate and analogs. The most preferred ones are methyl and ethyl (meth)acrylate.

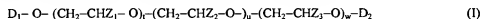
**[0041]** The associative monomer c) may be any compound falling within the above formula  $J-O-(CH_2-CHR_2O)_r-(CH_2)_s-R_1$  wherein R<sub>1</sub> and R<sub>2</sub> are as above indicated, the sum of r and s may vary between 0 and 80 and J is the acrylic residue of an ethylenically unsaturated acid selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids. Preferred are the esters of cetylstearylalcohol ethoxylated with 25 moles of ethylene oxide. The associative monomers c) are commercially available products, or they

can be prepared substantially according to procedures known in the art (U.S. Pat. Nos. 3,652,497 and 4,075,411).

**[0042]** The preferred ethylenically unsaturated amides d) are acrylamide, methacrylamide and vinylpyrrolidone, whereas the preferred ethylenically unsaturated sulfonic acids f) are vinylsulfonic acid and p-styrenesulfonic acid.

**[0043]** The crosslinking agents listed under point e) above can have one of the following structures of formula (I), (II) or (IV), or they are polyethoxylated derivatives of castor oil, optionally hydrogenated in whole or in part, esterified with ethylenically unsaturated carboxylic acids, with the proviso that the total number of ethylenic bonds is at least two.

The cross-linking agent e) is a compound of formula (I):



wherein:

D<sub>1</sub> and D<sub>2</sub>, which can be the same or different, are an ethylenically unsaturated acyclic residue, which may contain an additional carboxylic group wherein, optionally, said additional carboxylic group can be esterified with a (C<sub>1-20</sub>) aliphatic alkyl group;

Z<sub>1</sub> and Z<sub>3</sub> represent independently hydrogen or an (C<sub>1-20</sub>) aliphatic alkyl or aralkyl group;

Z<sub>2</sub> is hydrogen or methyl;

t and w are integers comprised between 0 and 20;

u is an integer comprised between 1 and 100;

the sum t+u+w may represent any integer comprised between 1 and 140;

with the proviso that, when Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> are simultaneously hydrogen and D<sub>1</sub> and D<sub>2</sub> are simultaneously the acryl residue of methacrylic acid, the sum t+u+w cannot be 1;

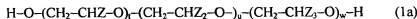
and wherein the structure of the polyalkyleneglycol may be random or block.

**[0044]** Preferably, in the crosslinking agents of formula (I), D<sub>1</sub> and D<sub>2</sub> represent, independently, the acyclic residue of acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic or linoleic acid, Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> represent hydrogen or methyl, the sum a+b+c is higher than 10 and the structure of the polyalkyleneglycol may be random or block.

[0045] More preferably, in the crosslinking agents of formula (I), D<sub>1</sub> and D<sub>2</sub> represent, independently, the acylic residue of acrylic, methacrylic or itaconic acid, Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> represent hydrogen, and the sum t+u+w is higher than 20.

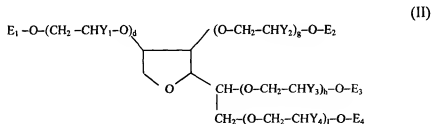
[0046] The crosslinking agents of formula (I) are products deriving from the esterification of polyalkyleneglycols with ethylenically unsaturated carboxylic acids; some of them are described in the literature (U.S. Pat. Nos. 3,639,459 and 4,138,381; DD Patent 205,891; Polymer, 1978, 19(9), 1067-1073; Pigm. Resin. Technol., 1992, 21(5), 16-17).

[0047] The compounds of formula (I) can also be prepared by esterification of the compounds of formula (Ia)



wherein, Z<sub>1</sub>, Z<sub>2</sub>, Z<sub>3</sub>, t, u and w are as above defined, with a carboxylic acid D<sub>1</sub>-OH and/or D<sub>2</sub>-OH, wherein D<sub>1</sub> and D<sub>2</sub> are as above defined, or the corresponding anhydride or acyl halide or, alternatively, by trans-esterification of the corresponding esters of low-boiling alcohols.

[0048] The crosslinking agent (e) is a compound of formula (II)



wherein:

E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent independently hydrogen or the acylic residue of a saturated or ethylenically unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>) aliphatic alkyl group, with the proviso that at least two of E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent ethylenically unsaturated acylic residues as above defined;

Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub>, which can be the same or different, are hydrogen, methyl or ethyl;

d, g, h and i are integers comprised between 0 and 30.

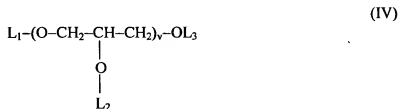
[0049] Preferably, the compounds of formula (II) are sorbitan derivatives (all of d, g, h and i are 0) or sorbitan derivatives ethoxylated with from about 4 to about 20 moles of ethylene oxide, in which at least two of the hydroxy groups are esterified with ethylenically unsaturated carboxylic acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids, and at least one of the two residual hydroxy groups is esterified with a fatty acid from 10 to carbon atoms.

[0050] The compounds of formula (II) are prepared by introducing the ethylenically unsaturated acyl groups as reported above in the preparation of the compounds of formula (I). The starting substrate is a compound of formula (II) wherein at least two of E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent hydrogen, and the remaining of E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> can be hydrogen or an acyl group as above defined.

[0051] The cross-linking agent e) may further be a polyethoxylated derivative of castor oil, optionally partially or totally hydrogenated, esterified with an ethylenically unsaturated carboxylic acid, with the proviso that, in said cross-linking agent, the total number of bonds of ethylenic type is at least two. Preferred are the polyethoxylated derivatives of castor oil with an ethoxylation degree varying from about 15 to about 150, esterified with acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.

[0052] These compounds are prepared by esterification of the corresponding polyethoxylated derivatives of castor oil, optionally partially or totally hydrogenated, following procedures known in the art.

[0053] The crosslinking agent e) may be a compound of formula (IV)



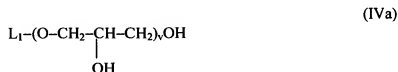
wherein:

L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>, which may be the same or different, are hydrogen or an acyl residue of a saturated or unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group,

with the proviso that at least two of L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> represent an ethylenically unsaturated acyclic residue as above defined;

p is an integer comprised between 2 and 50.

[0054] Also the compounds of formula (IV) are prepared through the above-illustrated conventional procedures, starting from a polyglycerol of formula



[0055] The cross-linked copolymers of the invention can be prepared by different polymerization procedures such as, for instance, the precipitation polymerization, suspension and solution polymerizations, or the emulsion polymerizations of the type oil-in-water or water-in-oil. The conditions of the polymerization reactions are, basically, those known in the art. Generally, the polymerizations are performed in the presence of anionic surfactants/emulsifiers, such as, for instance, sodium dodecylbenzenesulfonate, sodium disecundary-butyl naphthalene sulfonate, sodium laurylsulfate, sodium laurylether sulfate, disodium dodecyl diphenyl ether disulphonate, disodium n-octadecylsulfate, succinamate or sodium dioctylsulfosuccinate. Particularly preferred are sodium laurylsulfate and sodium laurylether sulfate. The temperature is generally comprised between about 50 and about 120°C., and the polymerization is completed in about 2-8 hours. The most preferred polymerization reaction is the oil-in-water emulsion polymerization.

[0056] The above-discussed class of thickeners are disclosed in greater detail in U.S. Patent 6,140,435 which disclosure is incorporated herein by reference.

[0057] Anionic polymeric rheology modifiers or thickening agents are available commercially from many suppliers under a variety of trade names. Thus, Noveon, Inc. (formerly The B.F. Goodrich Company) sells Carbopol® thickener resins in a variety of grades and products for various uses and applications. 3V/Sigma supplies a series of thickener products under the Synthalen® series, Stabylen®, PNC® and Polygel®. Rita sells the Acritamer® series of products. Pomponesco sells Addensante®, Gelacril® and Polacril® polymers. BASF sells Luvigel® and Sumitomo Seika sells Aqupec®. The following companies market their corresponding thickener polymers: Goldschmidt AG - TX®; Nihon

– Junlan®; Clariant – Aristoflex®; Alban Muller International – Amigel®; Corel Pharma Chem – Acrypol®; Elementis – Rheolate®; Wako Pure Chemical Ind. – Hiviswako®; Rhome & Haas – Aculyn® series; Ciba Specialty Chemicals – Salcare® series; ISP – Stabileze® series; National Starch and Chemical – Structure® series; and Seppic – Capigel® series, Sepigel® series and Simulgel® series.

#### **Other Additives**

[0058] Many personal care products may benefit from the use of complexed cationic ingredients of this invention if anionic polymeric rheology modifiers or thickeners are also employed in such products. Such personal care products are intended for use in the treatment of keratinous substances such as hair, nails, skin, lips or eyelashes. More specifically, they include various hair formulations such as shampoos, rinses, gels, dyes, preparations conditioners, mousses, hot oil treatment and products for shaping or styling hair, perming or straightening preparations, setting lotions and blow-drying lotions; skin creams, lotions and sanitizers; and products that are applied on the lips, nails and eyelashes. These personal care products usually will also contain additives to provide specific desirable properties for specific product application. Such additives are exemplified below, but other additional additives may also be used as needed or desired.

#### **Conditioning Agents:**

[0059] A personal care product containing a composition of the present invention also may include from about 0.1% to about 10%, particularly about 0.5% to about 10%, and preferably from about 1.0% to about 5.0%, by weight of a non-volatile silicone compound or other conditioning agent(s), preferably a water-insoluble, emulsifiable conditioning agent. The preferred non-volatile silicone compound is a polydimethylsiloxane compound, such as a mixture, in about a 3:1 weight ratio, of a low molecular weight polydimethylsiloxane fluid and a higher molecular weight polydimethylsiloxane gum. The non-volatile polydimethylsiloxane compound is added to the composition of the present invention in an amount sufficient to provide improved combing and improved feel (softness) to the hair.

[0060] Another type of a silicone conditioning agent is "silicone gums" which are those nonfunctional siloxanes having a viscosity of from about 5 to about 600,000 centistokes at 25°C. Preferred silicone gums include linear and branched polydimethylsiloxanes. Silicone



boiling point in the range of from about 100°C to about 300°C. Examples of volatile hydrocarbons useful in the composition of the present invention are the commercially-available compounds PERMETHYL 99A and PERMETHYL 101A, available from Permethyl Corporation, Frazer, Pennsylvania. A volatile hydrocarbon compound is useful in the composition of the present invention either alone, in combination with another volatile hydrocarbon, or in combination with a volatile silicone. Examples of other suitable water-insoluble conditioning agents that can be incorporated into the composition of the present invention include the following: polysiloxane polyether copolymers; polysiloxane polydimethyl dimethylammonium acetate copolymers; acetylated lanolin alcohols; lauryl dimethylamine oxide; a lanolin-derived extract of sterol or sterol esters; lanolin alcohol concentrate; an isopropyl ester of lanolin fatty acids; isopropyl ester of lanolin fatty acids; oleyl alcohol; stearyl alcohol; stearamidopropyl dimethyl myristyl acetate; a polyol fatty acid; a fatty amido amine; cetyl/stearyl alcohol; tris(oligoxyethyl)alkyl ammonium phosphate; an aminofunctional silicone; lapyrium chloride; isopropyl ester of lanolic acids; ethoxylated (30) castor oil; acetylated lanolin alcohol; fatty alcohol fraction of lanolin; a mineral oil and lanolin alcohol mixture; high molecular weight esters of lanolin; quaternium-75; vinylpyrrolidone/ dimethyl amino- ethylmethacrylate copolymer; 5 mole ethylene oxide adduct of soya sterol; 10 mole ethylene oxide adduct of soya sterol; stearic acid ester of ethoxylated (20 mole) methyl glucoside; sodium salt of poly-hydroxycarboxylic acid; hydroxylated lanolin; isostearamidopropyl dimethylamine lactate; isostearamidopropyl morpholine lactate; oleamidopropyl dimethylamine lactate; linoleamidopropyl dimethylamine lactate; stearamidopropyl dimethylamine lactate, ethylene glycol monostearate and propylene glycol mixture; stearamidopropyl dimethylamine lactate; cetearyl alcohol mixture; cetearyl alcohol; tallow imidazolium methosulfate; stearyl trimonium methosulfate; mixed ethoxylated and propoxylated long chain alcohols; stearamidopropyl dimethylamine lactate; polonitamine oxide; oleamine oxide; stearamine oxide; soya ethyldimonium ethosulfate; ricinoleamidopropyl ethyldimonium ethosulfate; N-(3-isostearamido- propyl)-N,N-dimethyl amino glycolate; N-(3-isostearamidopropyl)-N,N dimethyl amino gluconate; hydrolyzed animal keratin; ethyl hydrolyzed animal keratin; avocado oil; sweet almond oil, grape seed oil; jojoba oil; apricot kernel oil; sesame oil; hybrid safflower oil; wheat germ oil; cocamidoamine lactate; ricinoleamido amine lactate; stearamido amine lactate; stearamido morpholine lactate; isostearamido amine lactate; isostearamido morpholine lactate; wheat germamido dimethylamine lactate; behenamidopropyl betaine; ricinoleamidopropyl betaine;



wheat germamidopropyl dimethylamine oxide; disodium isostearaimido MEA sulfosuccinate; disodium oleamide PEG-2 sulfosuccinate; disodium oleamide MEA sulfosuccinate; disodium ricinoleyl MEA sulfosuccinate; disodium wheat germamido MEA sulfosuccinate; disodium wheat germamido PEG-2 sulfosuccinate; polyethylene glycol (400) mono and distearates; synthetic calcium silicate; isostearic alkanolamide; ethyl esters of hydrolyzed animal protein; blend of cetyl and stearyl alcohols with ethoxylated cetyl or stearyl alcohols; amido amines; polyamido amines; palmityl amido betaine; propoxylated (1-20 moles) lanolin alcohols; isostearamide DEA; and hydrolyzed collagen protein. When one or more of these water-insoluble conditioning agents is included in the composition of the present invention in an amount of about 0.5% to about 10% by total weight of the composition, the composition also can include a suspending agent for the conditioning agent, in an amount of about 0.5% to about 10%, by total weight of the composition. The particular suspending agent is not critical and can be selected from any materials known to suspend water-insoluble liquids in water. Suitable suspending agents are for example, distearyl phthalamic acid; fatty acid alkanolamides; esters of polyols and sugars; polyethylene glycols; the ethoxylated or propoxylated alkylphenols; ethoxylated or propoxylated fatty alcohols; and the condensation products of ethylene oxide with long chain amides. These suspending agents, as well as numerous others not cited herein, are well known in the art and are fully described in the literature, such as McCutcheon's Detergents and Emulsifiers, 1989 Annual, published by McCutcheon Division, MC Publishing Co. A nonionic alkanolamide also is optionally included in an amount of about 0.1% to about 5% by weight in the styling aid compositions that include a conditioning agent to provide exceptionally stable emulsification of water-insoluble conditioning agents and to aid in thickening and foam stability. Other useful suspending and thickening agents can be used instead of the alkanolamides such as sodium alginate; guar gum; xanthan gum; gum arabic; cellulose derivatives, such as methylcellulose, hydroxybutylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and carboxymethylcellulose; and various synthetic polymeric thickeners, such as the polyacrylic acid derivatives. Suitable alkanolamides include, but are not limited to, those known in the art of hair care formulations, such as cocamide monoethanolamide (MEA), cocamide diethanolamide (DEA), soyamide DEA, lauramide DEA, oleamide monoisopropylamide (MIPA), stearamide MEA, myristamide MEA, lauramide MEA, capramide DEA, ricinoleamide DEA, myristamide DEA, stearamide DEA, oleylamide DEA, tallowamide

DEA, lauramide MIPA, tallowamide MEA, isostearamide DEA, isostearamide MEA and combinations thereof.

**Neutralizing Agents:**

[0065] In formulations containing anionic rheology modifiers, it is often necessary to neutralize the polymeric thickener. Neutralization is accomplished with one or more inorganic bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide and/or ammonium carbonate. Useful neutralizing organic bases are primary, secondary and tertiary amines and the water soluble alkanol amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-methyl-2-amino-1-propanol (AMP), 2-amino-2-methyl-propanol and 2-amino-2-methyl-1,3-propanediol, respectively, 2-dimethylaminoethanol N,N-dimethyl- ethanolamine), 3-dimethylamino-1-propanol, 3-dimethylamino-2-propanol, 1-amino-2- propanol, and the like, monoamino glycols, and the like, which help solubilize the polymer in water solutions. The level of neutralization required varies for each polymer. The block copolymers become soluble in water and hydroalcoholic solutions at 20% to 100% neutralization, and at all described levels of water/alcohol/ propellant solutions. The pH of these solutions usually ranges from 4 to 12 but generally will be between 5 and 8. The lowest neutralization level needed to render the polymer water soluble or dispersible depends on the composition of the block polymer, and the amount of alcohol, water, and propellant.

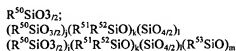
**Aerosol Propellant Gas:**

[0066] The propellant gas included in aerosol compositions can be any liquefiable gas conventionally used for aerosol containers. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoro- methane, trichlorotrifluoroethane, dimethyl ether, propane, n-butane and isobutane, used singly or admixed. Water-soluble gases such as dimethyl ether, carbon dioxide, and/or nitrous oxide also can be used to obtain aerosols having reduced flammability. Water-immiscible, liquified, hydrocarbon and halogenated hydrocarbon gases such as propane, butane and chlorofluorocarbons can be used advantageously to deliver the contents of the aerosol container without the dramatic pressure drops associated with other immiscible gases. Here there is no concern for the head space to be left inside the aerosol container, because the liquified gas will sit on top of the aqueous formulation and the

pressure inside the container is always the vapor pressure of saturated hydrocarbon vapor. Other insoluble, compressed gases such as nitrogen, helium and fully-fluorinated oxetanes and oxepanes also are useful to deliver the compositions from aerosol containers. Other means of delivery of the above-described aqueous styling aid compositions include, pump sprayers, all forms of bag-in-can devices, in situ carbon dioxide (CO<sub>2</sub>) generator systems, compressors, and the like. The amount of the propellant gas is governed by normal factors well known in the aerosol art. For mousses, the level of propellant is generally from about 3% to about 30%, preferably from about 5% to about 15% of the total composition. If a propellant such as dimethyl ether utilizes a vapor pressure suppressant (e.g., trichlorethane or dichloromethane), for weight percentage calculations, the amount of suppressant is included as part of the propellant.

[0067] The final products may optionally contain one or more fixative resins. Examples of hair fixative resins include synthetic polymers such as polyacrylates, polyvinyls, polyesters, polyurethanes, polyamides and mixtures thereof; polymers derived from natural sources such as modified cellulose, starch, guar, xanthan, carragenan and blends thereof. These resins may have cationic, anionic, nonionic, ampholytic or zwitterionic in character. They may be soluble, dispersible or insoluble in water and hydroalcoholic formulations glass transition temperature, T<sub>g</sub>, may be in the range from -50°C to 200°C.

[0068] Another class of organosilicones that may be advantageously incorporated in hair styling compositions are silicone resins which are non-polar silsesquioxanes. These resins are film forming and aid in imparting good cure retention property to the composition. The silsesquioxanes have a formula selected from the group consisting of



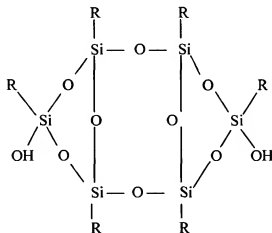
and hydroxy, alkoxy, aryloxy, and alkenoxy, derivatives thereof, wherein R<sup>50</sup>, R<sup>51</sup>, R<sup>52</sup> and R<sup>53</sup>, are selected from the group consisting of alkyl, alkenyl, aryl, and alkylaryl, radicals having from one to twenty carbon atoms; and j, k, l, and m, are each integers having a value of from zero to about one thousand, with the proviso that the sum of integers j and l must be at least one.

[0069] The nonpolar silsesquioxane silicone resin materials conforming to any one of the above-specified generic formulas are commercially available from the Dow Corning Corporation, Midland, Michigan.

[0070] These nonpolar silsesquioxanes can be incorporated into hair styling formulations containing the block copolymers of the invention provided a solvent, such as ethanol or any other appropriate solvent is present in the formulation, either above or in a mixture with water.

[0071] The organosilicone compound is present in the mixture at a level from about 0.1 to about fifty percent by weight based on the weight of the mixture. Preferably, the organosilicone compound is present in the mixture at a level from about three to about thirty percent by weight based on the weight of the mixture. The solvent may be water, a hydrocarbon, an alcohol, or a blend of alcohol and water. Other solvents which may be employed include supercritical fluids such as supercritical carbon dioxide and nitrogen; volatile silicones including linear and cyclic siloxanes; non-volatile hydrocarbons; and in some instances, aqueous emulsion systems may also be appropriate. Where the solvent is hydrocarbon, it is preferred to employ materials such as dimethylether, liquefied petroleum gas, propane, and isobutane. In the event the solvent is an alcohol, some appropriate materials are methanol, ethanol, and isopropanol.

[0072] One example of a silsesquioxane may be represented by the formula



[0073] Another additive that may be incorporated is a soluble surface tension reducing compound. It is any soluble compound which reduces the surface tension between the hair styling composition and the gaseous atmosphere above the hair styling composition. By "gaseous atmosphere" we mean a propellant or air. The soluble surface tension reducing compound may be for example a plasticizer or surfactant in a hair styling composition. The soluble surface tension reducing compound includes for example dimethiconopolys, panthenol, fluorosurfactants, glycerin POE, PPG 28 Buteth 35, PEG 75 lanolin, octoxynol-9, PEG-25 hydrogenated castor oil, polyethylene glycol 25 glyceryl trioleate, oleth-3 phosphate, PPG-5-ceteth-10 phosphate, PEG-20 methyl glucose ether, or glycereth-7-triacetate, glycereth-7-benzoate or combinations thereof. Preferably the soluble surface tension compound is dimethiconopolys, panthenol, glycereth-7-benzoate, or combinations thereof.

[0074] The soluble surface tension reducing compound is typically present in the low beading, low VOC hair styling composition at a concentration of from 0.01 to 1 weight percent, and more preferably at a concentration of from 0.01 to 0.25 weight percent, based on the total weight of the composition.

[0075] Also useful additives are plasticizing compounds. The first class of plasticizing compounds are soluble polycarboxylic acid esters. The polycarboxylic acid esters have a carbon backbone of from 3 to 12 carbon atoms and 3 or more C<sub>1</sub> to C<sub>5</sub> alkyl carboxylate groups attached thereto. Suitable polycarboxylic acid esters include, for example, triethyl citrate, tributyl citrate, triethyl phthalate, tributyl phthalate, triphenyl phthalate or combinations thereof. Preferably, the polycarboxylic acid esters are selected from triethyl citrate, tributyl citrate, tributyl phthalate, or combinations thereof and more preferably are selected from triethyl citrate, tributyl citrate, or combinations thereof. The plasticizing compounds are preferably added to a hair styling composition to provide a total concentration of from 0.01 to 1.0 weight percent plasticizing compounds, more preferably 0.1 to 0.5 weight percent plasticizing compounds, based on the total weight of a hair styling composition.

[0076] The formulation may optionally contain one or more nonactive adjuvants in an amount up to about 5 wt. % based on the total composition. Such nonactive additives include a corrosion inhibitor, a surfactant, a film hardening agent, a hair curling agent, a coloring

agent, a lustrant, a sequestering agent, a preservative and the like. Typical corrosion inhibitors include methylethyl amine borate, methylisopropyl amine borate, inorganic hydroxides such as ammonium, sodium and potassium hydroxides, nitromethane, dimethyl oxazolidine, 2-dimethylamino-2-methyl-1-propanol, and aminomethyl propanol.

[0077] Emollients like Guerbet alcohols and esters thereof, silicone derivatives, beeswax, C12-15 alcohols, benzoate, mineral oil, capric triglycerides, cetearyl alcohol, cetearth-20, castol oil, isohexadecane, isopropyl myristate, isopropyl palmitate, cetearyl octanoate and petrolatum;

[0078] UV-absorbers like butyloctyl salicylate, octylmethoxycinnamate, avobenzone, benzophenone-3 and benzophenone-4, octyl salicylate, para-aminobenzonic acid (PABA), octyldimethyl PABA, hindered cyclic amine UV-light stabilizers based on 3,5-hindered piperidines available as TINUVIN® series of products from Ciba Specialty Chemicals or 3,5-hindered-2-keto-piperazinones.

[0079] Surfactants like alcohols, alcohol ethoxylates, alkanolamine-derived amides, ethoxylated amides, amine oxides, ethoxylated carboxylic acids, ethoxylated glycerides, glycol esters and derivatives thereof, monoglycerides, polyglyceryl esters, polyhydric alcohol esters and ethers, sorbitan/sorbitol esters, trimesters of phosphoric acid, ethoxylated lanolin, silicone polyethers, PPO/PEO ethers, alkylpolyglycosides, acyl/dialkyl ethylenediamines and derivatives, n-alkyl amino acids, acyl glutamates, acyl peptides, sarcosinates, taurates, alkanolic acids, carboxylic acid esters, carboxylic acid ethers, phosphoric acid esters and salts, acyl isethionates, alkylaryl sulfonates, alkyl sulfonates, sulfosuccinates, alkyl ether sulfates and alkyl sulfates.

#### **Carrier Vehicle:**

[0080] Polar solvents are typically used to prepare the cosmetic or hair compositions. Water, glycols and alcohols are preferably used. The optional alcohol employed in the composition is an aliphatic straight or branched chain monohydric alcohol having 2 to 4 carbon atoms. Isopropanol and especially ethanol are preferred. The concentration of the alcohol in the composition should be less than about 40% by weight, and surprisingly can be

as low as 0%, preferably 0-30% by weight and more preferably 5-20% by weight. Some alcohol, in an amount of about 2% to about 10% by weight.

[0081] A non-aerosol, low VOC, pump hair spray composition is provided herein which is capable of being applied by the user as a fine spray mist, which dries rapidly on the hair, and which provides low curl droop and effective curl retention properties thereon. The composition consists essentially of a copolymer as a hair fixative polymer, and a mixture of alcohol, water and dimethoxymethane (DMM) as cosolvents therefor. Such formulations may be prepared as anhydrous formulas as well as all water systems, and both as hair sprays or as mousse products. For these applications, it is preferable to use lower molecular weight hair fixative copolymers and the sprayed droplets size should be as small as practical to achieve fast drying of the film. Preferably, the hair fixative polymer is present at a solids level of about 1-15%, the alcohol in an amount of about 50-70%, water at 10-30%, and DMM at 10-30%, by weight of the composition.

## **COMPATIBILITY OF COMPLEXED CATIONICS WITH CARBOPOL® POLYMERS**

### **Experimental**

[0082] A 0.5% Carbopol® polymer mucilage was prepared and neutralized to pH 7.0-7.5 with sodium hydroxide (PART A). Separately, a solution containing the appropriate levels of cationic material, silicone and neutralizing agent (sodium hydroxide or citric acid, to pH 7.0-7.5) was prepared (PART B). Twenty parts PART B was added to eighty parts PART A. Viscosity was measured on a Brookfield RV Viscometer at 23°C and 20 rpm. Turbidity was measured on a Micro 1000 Turbidimeter.

### **Results and Discussion**

[0083] Figures 1-3 show low molecular weight quaternary ammonium compounds (cetrimonium chloride, stearammonium chloride and olealkonium chloride) complexed with Ultrasil™ CA-1 silicone (dimethicone copolyol phthalate or DMC phthalate), and added to a Carbopol® ETD 2020 polymer mucilage. As the level of Ultrasil™ CA-1 silicone was increased, the viscosity increased and turbidity trended toward that of a gel containing no cationic material whatsoever. When enough anionic silicone was used, precipitate was no

longer generated. A dotted line in the Figures signifies presence of precipitate. Conversely, a solid line signifies absence of precipitate.

**[0084]** This concept is broad in scope and applies to a wide range of Carbopol® polymers and anionic silicones, evidenced by Figures 4-6. Figure 4 shows the results of a DMC succinate-stearalkonium chloride complex in a mucilage made with Carbopol® 980 polymer. Figure 5 shows the results of a DMC sulfate-olealkonium chloride complex in a mucilage made with Carbopol® Ultrez-21 polymer. Figure 6 shows the results of a DMC phosphate-cetrimonium chloride complex in a mucilage made with Carbopol® ETD 2050 polymer (acrylates/C10-30 alkyl acrylated crosspolymer). Viscosity was not recovered in all cases, but turbidity reduction was common to all of the examples. Precipitation elimination was common to all of examples except for the system depicted in Figure 6, which showed no precipitation at any of the tested conditions. Some systems (Figure 5) required more silicone to achieve the desired effect.

**[0085]** Cationic ingredients are typically used at lower pH values (4-6). Gels with minimum ingredients, such as those studied in Figures 1-6, are very sensitive at low pH values and produce curves that are too noisy to clearly show trends. While Figures 1-6 are valuable for academic purposes, more practical demonstrations of the ability of anionic silicones to compatibilize cationics and Carbopol® polymers are shown below in FORMULATIONS.

**[0086]** Additional testing (Table 1) shows that the dimethicone copolyol precursor to Ultrasil™ CA-1 silicone has very limited capacity to compatibilize the cationic ingredient and the thickener when compared to CA-1. This demonstrates that the observed compatibilization is due to complexation, and not steric effects of the silicone.



**Table 1. Compatibility of Low MW Quats in a Gel Containing 0.4% Carbopol® ETD 2020 Polymer at pH 7.0-7.5**

Ultrasil™ CA-1 Silicone, %	Dimethicone Copolyol %	Cetrimonium Chloride %	Stearalkonium Chloride, %	Viscosity, mPa·s	Turbidity, NTU	Precipitate
-	-	0.30	-	12,200	487	Yes
-	0.50	0.30	-	2,650	459	Yes
0.50	-	0.30	-	15,200	13.1	No
-	-	-	0.30	10,500	>10,000	Yes
-	0.50	-	0.30	9,150	164	Yes
0.50	-	-	0.30	11,750	22.1	No

NOTE: A neutral gel containing only 0.4% Carbopol® ETD 2020 polymer and sodium hydroxide was measured to have a viscosity of 13,700 mPa·s and a turbidity of 3.8 NTU.

[0087] Enhanced compatibility with Carbopol® polymers does not appear to be limited to low MW quaternary ammonium compounds. Polyquaternium compounds and divalent cations were screened, with positive results (Table 2).

**Table 2. Compatibility of Polyquaternium Compounds and Divalent Cations in a Gel Containing 0.4% Carbopol® ETD 2020 Polymer at pH 7.0-7.5**

Ultrasil™ CA-1 Silicone, %	Cationic Material	Active Cationic Material, %	Viscosity, mPa·s	Turbidity, NTU	Precipitate
-	Polyquaternium-7*	0.30	11,000	11.2	Yes
0.50	Polyquaternium-7*	0.30	8,100	10.3	No
-	Polyquaternium-11†	0.30	16,100	7.7	Yes
0.50	Polyquaternium-11†	0.30	12,650	7.4	No
-	Calcium Acetate Monohydrate (Fisher)	0.10	7,400	6.7	Yes
0.15	Calcium Acetate Monohydrate (Fisher)	0.10	5,700	4.7	No

NOTE: A neutral gel containing only 0.4% Carbopol® ETD 2020 and sodium hydroxide was measured to have a viscosity of 10,200 mPa·s and a turbidity of 4.1 NTU.  
\* Merquat 550 from Nalco † Gafquat 734 from ISP

[0088] Without the inclusion of the Ultrasil™ CA-1 silicone, the addition of polyquaternium compound or multivalent cation resulted in precipitation. When CA-1 was included in the preparation of the sample, no precipitate was present, and the viscosity readings were reduced. This reduction in viscosity is an indication of reduced “ionic crosslinking” of Carbopol® polymer by the tested cationic materials. Turbidity was already very low at the tested conditions and seemed to be unaffected by CA-1 inclusion.

[0089] In general, the best results were observed when the silicone and the cationic material were blended in aqueous media, adjusted to match the pH of gel, and finally added

to the gel. The appropriate silicone-to-cationic ratio was found to be formulation dependent. It increases as the usage level of the cationic is raised, and as the pH decreases.

### Conclusions

[0090] Low molecular weight quaternary ammonium compounds, when complexed with anionic silicones, can be made compatible with systems containing Carbopol® polymer. Increased compatibility is defined as reduced tendency to form precipitation, reduced turbidity, and/or improvement in viscosity profile. Anionic silicones also compatibilize Carbopol® polymers with polyquaternium compounds and divalent cations.

### EFFICACY

[0091] The following tests show that complexation of the cationic material does not interfere with the ability of the cationic material to deposit on anionic hair. Such interference would negatively affect conditioning properties such as wet comb-through, for which low MW quats are most commonly used to improve.

[0092] The Rubine dye test is commonly used to measure deposition of cationic ingredients on hair. It involves soaking pre-conditioned yak hair in a solution of anionic red dye. Yak hair is used because of its availability and lack of color. The hair's uptake of red dye is related to the amount of cationic material already deposited. A colorimeter measures hair color according to the CIE-LAB ternary coordinate system. Positions on the three dimensionless axes ( $L^*$ =lightness,  $a^*$ =red-green and  $b^*$ =yellow-blue), which correspond to color differences perceived by human vision, are assigned based on the reflectance spectrum of the hair sample. The  $a^*$  axis is used to gauge the uptake of red dye.

[0093] Wet comb-through is the total work required to pull the wet hair completely through a comb five times, as measured by a tensiometer.

### Experimental

#### *Rubine Dye Test*

[0094] Clipped yak belly hair tresses (about 3g, 18cm each) from International Hair Importers, Inc. were washed with a 10% solution of sodium lauryl sulfate. Background color scans were taken using a Hunter LabScan II Colorimeter with Universal Software V.2.10. The tresses were dampened with DI water, soaked in a solution of conditioner for a total of

three minutes and rinsed for one minute with lukewarm tap water. Excess water was wrung out. The tresses were soaked in a solution of 0.5% pyrazol dye (pH 3.5 with acetic acid) for five minutes, and again rinsed for one minute using lukewarm tap water. The tresses were allowed to dry at room temperature. Color measurements were repeated. Tests were performed in duplicate.

#### *Wet Comb-Through Test*

[0095] Bleached Virgin European brown clipped human hair tresses (about 3g, 18cm each) from International Hair Importers, Inc. were washed with a 10% solution of sodium lauryl sulfate. The tresses were dampened with DI water, soaked in a solution of conditioner for a total of three minutes, and rinsed for one minute with lukewarm tap water. Each wet tress was placed in an A/TG tensile grip of a TA-XT2I Texture Analyser (Texture Technology Corp.) at 23°C and 50% relative humidity. The tensile grip was lowered so that the hair rested in the designated section of the exposed fine tines of the comb (model 220041 from Sally's Beauty Supply). The tress was raised at a rate of 3.0 mm/s until it had completely passed through the comb. The force needed to raise the tress was recorded as a function of distance. This was repeated four times, for a total of five pulls. The areas under the force vs. distance curves were calculated and summed, yielding total work performed. Tests were performed in triplicate.

#### **Results and Discussion**

[0096] Figures 7-9 show the results of Rubine dye tests.

[0097] Figure 7 shows the hair treated with a conditioning system comprising cetrimonium chloride complexed with Ultrasil™ CA-1 silicone. A conditioning system comprising the same quaternary compound blended with the dimethicone copolyol precursor to CA-1 was also tested (this is the exact same conditioning system, without the ability to complex). No significant deposition difference was observed between the two conditioning systems, which suggests complexation does not affect cationic deposition on hair. A conditioning system consisting only of cetrimonium chloride deposited slightly better than the other two, which can be attributed to the absence of steric effects from other ingredients.

[0098] Figure 8 shows similar results with stearammonium chloride. Again, complexation is shown to not reduce deposition. In fact, more deposition was measured with the silicone-complexed conditioning system than with the silicone-blended conditioning system.

[0099] Figure 9 shows no significant differences between three olealkonium chloride conditioning systems. Although differences were measured, they were of roughly the same magnitude as the differences between duplicate tresses for a given conditioning system.

[00100] Two conditioning systems (cetrimonium chloride complexed with dimethicone copolyol phthalate, Ultrasil CA-1, which is anionic, and cetrimonium chloride blended with dimethicone copolyol, the precursor to CA-1, which is not anionic) whose cationic components deposit equally on hair (as shown by the Rubine dye tests) were shown to perform differently in wet comb-through tests (Figure 10). The silicone complex had better comb-through than the silicone blend, both of which had better comb-through than a simple cetrimonium chloride solution. The differences can be attributed to differing levels of silicone on the hair. It can be concluded that not only does cationic material that has been complexed still deposit on the hair, but it brings the anionic silicone along with it, in quantities greater than the anionic silicone would otherwise deposit (assuming anionic silicone and dimethicone copolyol have similar deposition on hair). This conclusion is supported by Figure 11, which shows the same experiment run on stearalkonium chloride. The stearalkonium tests showed much greater tress-to-tress variation, but the overall conditioning system rankings were the same as with cetrimonium chloride.

### Conclusions

[00101] Complexing low MW quaternary ammonium compounds with anionic silicone does not reduce the deposition of the quat onto hair, but appears to increase the deposition of silicone onto hair which enhances conditioning properties.

## FORMULATIONS

### Clear Conditioning Styling Gel

[00102] This crystal clear formula contains cetrimonium chloride, Ultrasil™ CA-1 silicone and Carbopol® ETD 2020 polymer. It demonstrates the utility of complexation at realistic pH levels.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
<b>Part A</b>			
Deionized Water	QS	Diluent	Carbopol® ETD 2020 Polymer (Noveon)
Acrylates/C10-C30 Alkyl Acrylates	0.55	Rheology Modifier	
Crosspolymer			
Sodium Hydroxide (10%)	0.20	Neutralizing Agent	
<b>Part B</b>			
Deionized Water	12.0	Diluent	Luviskol® VA 73W (BASF)
VP/VA Copolymer	7.50	Fixative	
Sodium Hydroxide (1%)	0.20	Neutralizing Agent	
<b>Part C</b>			
Deionized Water	2.50	Diluent	Uvinul® MS-40 (BASF)
Benzophenone-4	0.05	UV Absorber	
<b>Part D</b>			
Deionized Water	2.50	Diluent	Versene NA (Dow)
Disodium EDTA	0.05	Chelating Agent	
<b>Part E</b>			
Deionized Water	12.0	Diluent	Ultrasil™ CA-1 Silicone (Noveon)
Dimethicone PEG-7 Phthalate	0.10	Conditioner/Compatibilizing Agent	
		Conditioner	
Cetrimonium Chloride (30%)	0.20		
<b>Part F</b>			
DMDM Hydantoin	0.30	Preservative	Glydant® (Lonza)
Sodium Hydroxide (10%)	QS to pH 5.0-5.3	Neutralizing Agent	

Procedure:

Part A was prepared – Carbopol® ETD 2020 polymer was sifted into water and neutralized. Part B was prepared and added to Part A. Part C was prepared and added. Part D was prepared using heat and added. Part E was prepared and added. The ingredients of Part F were added separately.

Properties of Styling Gel

pH	5.3
Viscosity @ 20 rpm, 20C (mPa·s)	16,400
Turbidity on Micro 1000 Turbidimeter (NTU)	8
Stability	Passed 3 months accelerated, 45°C
Freeze-Thaw Stability (3 cycles)	Pass

[00103] When preparation of the preceding formulation was repeated without Ultrasil™ CA-1 silicone, precipitate formed immediately upon addition of the cetrimonium chloride.

**Clear Rinse-Off Conditioning Gel**

[00104] This unique rinse-off formula contains cetrimonium chloride, dimethicone copolyol sulfate and Carbopol® ETD 2020 polymer. It shows how complexation can be used to make formulations that would otherwise not be possible.

Ingredient	Weight %	Function	Trade Name (Supplier)	
<b>Part A</b>				
Deionized Water	QS	Diluent	Carbopol® ETD 2020 Polymer (Noveon)	
Acrylates/C10-C30 Alkyl	0.50	Rheology Modifier		
Acrylates Crosspolymer	0.55 (QS to pH 5.0-5.3)	Neutralizing Agent		
Sodium Hydroxide (18%)				
<b>Part B</b>				
Cetrimonium Chloride (30%)	0.50	Conditioner	Genamin CTAC (Clariant)	
Dimethicone PEG-7 Sulfate (35%)	1.50	Conditioner/Compatibilizing Agent	Ultrasil™ SA-1 Silicon (Noveon)	
Deionized Water	2.50	Diluent		
Citric Acid (50%)	0.10 (QS to pH 5.0-5.3)	Neutralizing Agent		
<b>Part C</b>				
Benzophenone-4	0.05	UV Absorber	Uvinul MS-40 (BASF)	
Silicone Quaternium-8	2.00	Conditioner	Ultrasil™ Q-8 Silicone	
DMDM Hydantoin	0.30	Preservative	Glydant® (Lonza)	
FD&C Yellow #5 (0.1%)	0.07	Dye	(Noveon Hilton Davis)	
FD&C Blue #1 (0.1%)	0.07	Dye	(Noveon Hilton Davis)	
<b>Part D</b>				
Fragrance	0.20	Fragrance	Country Apple 354-06 (Drom)	
Polysorbate 20	0.20	Solubilizing Agent	Tween 20 (Uniqema)	

**Procedure:**

Part A was prepared – Carbopol® ETD 2020 polymer was sifted into water and neutralized. Part B was blended and added to Part A. Part C ingredients were added one at a time. Part D was blended and added.

**Properties of Conditioning Gel**

pH	5.2
Viscosity @ 20 rpm, 20C (mPa·s)	12,400
Turbidity on Micro 1000 Turbidimeter (NTU)	20
Stability	Passed 3 months accelerated, 45°C
Freeze-Thaw Stability (3 cycles)	Pass

**[00105]** When preparation of the preceding formulation was repeated without dimethicone copolyol sulfate, the final product form contained precipitate.

**Clear Conditioning Styling Gel**

**[00106]** This clear styling gel formula contains Polyquaternium-4, dimethicone copolyol succinate and Carbopol® Ultrez 21 polymer. It demonstrates the utility of the complexation in formulations containing polyquaternium compounds.

<b>Ingredient</b>	<b>Weight Percent</b>	<b>Function</b>	<b>Trade Name (Supplier)</b>
<b><u>Part A</u></b>			
Deionized Water	67.5	Diluent	
Acrylates/C10-C30 Alkyl	0.30	Rheology	Carbopol® Ultrez 21
Acrylates Crosspolymer		Modifier	Polymer (Noveon)
DMDM Hydantoin	0.30	Preservative	Glydant® (Lonza)
Aminomethyl Propanol	0.25 (QS to pH 6.8-7.0)	Neutralizing Agent	AMP-95 (Angus)
<b><u>Part B</u></b>			
Deionized Water	29.0	Diluent	
Polyquaternium-4	1.00	Fixative	Celquat® H-100 (National Starch)
	1.00	Conditioner / Compatibilizing Agent	Ultrasil™ CA-2 Silicone
Dimethicone PEG-7 Succinate			
Aminomethyl Propanol	0.25 (QS to pH 6.8-7.0)	Neutralizing Agent	AMP-95® (Angus)

**Procedure:**

Part A was prepared – Carbopol® Ultrez 21 polymer was added into water and allowed to wet. Glydant was added. Neutralizer was added. Part B was prepared – Polyquaternium-4 was sifted into water and mixed until uniform. CA-2 was added, and Part B was neutralized. Part B was added to Part A.

**Properties of Styling Gel**

pH	6.9
Viscosity @ 20 rpm, 20C (mPa·s)	17,550
Turbidity on Micro 1000 Turbidimeter (NTU)	6.9
Stability	Passed 3 months accelerated, 45°C

**[00107]** When preparation of the preceding formulation was repeated without dimethicone copolyol succinate, the final product viscosity was higher (40,000 mPa·s), but the turbidity (14.5 NTU) was not optimal.

**Aloe Gel**

**[00108]** This skin moisturizer formula contains aloe extract, dimethicone copolyol succinate and Carbopol® Ultrez 21 polymer. It demonstrates the utility of the complexation in formulations containing high levels of salts.

Ingredient	Weight Percent	Function	Trade Name (Supplier)
<b>Part A</b>			
Deionized Water	86.4	Diluent	
Acrylates/C10-C30 Alkyl	0.80	Rheology Modifier	Carbopol® Ultrez 21
Acrylates Crosspolymer			Polymer (Noveon)
DMDM Hydantoin	0.30	Preservative	Glydant® (Lonza)
Sodium Hydroxide (18%)	0.60	Neutralizing Agent	
<b>Part B</b>			
Deionized Water	6.60	Diluent	
Dimethicone PEG-7 Succinate	1.00	Conditioner /	Ultrasil™ CA-2 Silicone
		Compatibilizing Agent	
Aloe Vera Gel (40:1)	2.50	Moisturizer	Aloe Vera Gel Decolorized, 40X (Terry Labs)
Sodium Hydroxide (18%)	0.50 (QS to pH 6.9-7.1)	Neutralizing Agent	
<b>Part C</b>			
Sodium Hydroxide (18%)	0.50 (QS to pH 6.5-6.7)	Neutralizing Agent	

**Procedure:**

Part A was prepared – Carbopol® Ultrez 21 polymer was added to water and allowed to wet. Glydant was added. Neutralizer was added. Part B was blended. Part B was added to Part A. Mixture was neutralized

**Properties**

pH	6.6
Viscosity @ 20 rpm, 20C (mPa·s)	12,750
Turbidity on Micro 1000 Turbidimeter (NTU)	4.3
Stability	Passed 3 months accelerated, 45°C

[00109] When preparation of the preceding formulation was repeated without dimethicone copolyol succinate, the final product viscosity was higher (18,200 mPa·s), but the turbidity (15.5 NTU) was not optimal.

**DATA FOR FIGURES****Data for Figure 1.**

Percent Ultrasil™ CA-1 Silicone	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	12,200	487	Yes
0.3	13,500	120	Yes
0.5	15,200	13.1	No
1.0	16,000	11.9	No
Mucilage viscosity and turbidity is 13,700 mPa·s and 3.8 NTU, respectively.			



**Data for Figure 2.**

Percent Ultrasil™ CA-1 Silicone	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	10,500	> 10,000	Yes
0.2	8,850	99.5	Yes
0.3	10,000	99.7	Yes
0.5	11,750	22.1	No
0.8	11,250	22.6	No
1.0	14,100	34.7	No
Mucilage viscosity and turbidity is 13,700 mPa·s and 3.8 NTU, respectively.			

**Data for Figure 3.**

Percent Ultrasil™ CA-1 Silicone	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	17200	889	Yes
0.2	17300	66.3	Yes
0.3	21100	58.1	Yes
0.5	21050	19.5	Yes
0.8	26700	12.9	No
1.0	27300	13.0	No
Mucilage viscosity and turbidity is 13,000 mPa·s and 4.8 NTU, respectively.			

**Data for Figure 4.**

Percent DMC Succinate	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	8,180	> 10,000	Yes
0.2	7,160	> 10,000	Yes
0.3	6,220	> 10,000	Yes
0.5	6,160	1083	Yes
0.8	4,500	811	No
1.0	4,200	202	No
Mucilage viscosity and turbidity is 31,800 mPa·s and 7.9 NTU, respectively.			

**Data for Figure 5.**

Percent	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	8700	1159	Yes
0.2	10200	325	Yes
0.3	10200	198	Yes
0.5	10350	75.1	Yes
0.8	11200	39.4	Yes
1.0	11050	30.1	Yes
1.5	12000	26.9	Yes
2.0	12150	27.2	Yes
3.0	12100	27.6	No
3.5	11400	27.6	No
4.0	12100	22.8	No
Mucilage viscosity and turbidity is 31,900 mPa·s and 3.4 NTU, respectively.			

**Data for Figure 6.**

Percent	Viscosity (mPa·s)	Turbidity (NTU)	Precipitate
0	1,500	> 10,000	No
0.2	1,020	2,112	No
0.3	1,090	1,351	No
0.5	1,010	891	No
0.8	1,010	34.5	No
1.0	1,090	21.8	No
Mucilage viscosity and turbidity is 3,670 mPa·s and 10.6 NTU, respectively.			

**Data for Figure 7.**

	Control	1% Cetrimonium Chloride	1% Cetrimonium Chloride, 1.67% Dimethicone Copolyol	1% Cetrimonium Chloride, 1.67% Dimethicone Copolyol Phthalate
Tress 1	17.63	25.51	23.58	23.57
Tress 2	20.94	23.76	-	23.02
Avg.	19.3	24.6	23.6	23.3

**Data for Figure 8.**

	Control	1% Stearalkonium Chloride	1% Stearalkonium Chloride, 1.67% Dimethicone Copolyol	1% Stearalkonium Chloride, 1.67% Dimethicone Copolyol Phthalate
Tress 1	17.63	30.87	25.99	28.45
Tress 2	20.94	31.50	-	27.13
Avg.	19.3	31.2	26.0	27.8

**Table IX. Data for Figure 9.**

	Control	1% Olealkonium Chloride	1% Olealkonium Chloride, 1.67% Dimethicone Copolyol	1% Olealkonium Chloride, 1.67% Dimethicone Copolyol Phthalate
Tress 1	14.94	24.87	26.60	24.66
Tress 2	14.59	24.95	24.22	23.82
Avg.	14.8	24.9	25.4	24.2

**Data for Figure 10. All values of work in g·cm.**

	1%Cetrimonium Chloride	1% Cetrimonium Chloride, 1.67% Dimethicone Copolyol	1% Cetrimonium Chloride, 1.67% Dimethicone Copolyol Phthalate
<b>Unconditioned</b>			
Tress 1	2,467 1,508 1,280 1,375 891	3,577 1,524 1,396 1,026 1,111	3,682 2,054 1,402 1,004 1,163
(Total)	7,521	8,634	9,305
Tress 2	2,792 1,150 730 891 1,226	2,160 1,007 898 596 578	4,177 1,312 906 826 606
(Total)	6,789	5,234	7,827
Tress 3	7,639 5,598 2,803 1,791 1,502	2,645 1,128 1,859 1,308 1,083	6,465 1,765 1,680 1,062 1,295
(Total)	19,333	4,856	12,267
<b>Conditioned</b>			
Tress 1	1,435 1,503 1,021 997 1,016	909 759 651 552 768	1,191 553 654 542 423
(Total)	5,972	3,639	3,413
% Con.	(79.4)	(42.1)	(36.7)
Tress 2	1,598 822 766 789 639	817 605 423 497 455	604 538 395 354 338
(Total)	4,614	2,797	2,229
% Con.	(68.0)	(53.3)	(28.5)
Tress 3	3,186 1,912 1,662 1,240 872	1,227 612 - - 466	541 481 574 531 503
(Total)	8,832	2,305	2,630
% Con.	(45.7)	(47.5)	(21.4)
% Con. (Avg)	(64.4)	(47.7)	(28.9)

Data for Figure 11. All values of work in g·cm.

	Stearalkonium Chloride, 1%	1% Stearalkonium Chloride, 1.67% Dimethicone Copolyol	1% Stearalkonium Chloride, 1.67% Dimethicone Copolyol Phthalate
Unconditioned			
Tress 1	3,201	2,823	1906
	1,134	921	1074
	1,004	881	833
	894	527	1013
	912	654	860
(Total)	7,145	5,806	5686
Tress 2	3,967	1,158	2011
	2,812	695	1142
	2,758	426	825
	1,576	769	777
	1,269	521	592
(Total)	12,391	3,569	5347
Tress 3	2,471	4,314	2681
	819	3,740	1323
	943	2,317	893
	694	1,716	846
	616	1,286	1156
(Total)	5,543	13,373	6899
Conditioned			
Tress 1	1,644	1,288	1,143
	1,069	859	525
	822	415	557
	845	450	551
	628	384	440
(Total)	5,008	3,396	3,216
% Con.	(70.1)	(58.5)	(56.6)
Tress 2	3,854	1,019	856
	876	560	597
	534	909	463
	462	770	559
	330	634	505
(Total)	6,056	3,892	2,980
% Con.	(48.9)	(109.1)	(55.7)
Tress 3	2,826	841	927
	1,055	611	632
	924	489	527
	584	639	423
	415	582	506
(Total)	5,804	3,163	3,015
% Con.	(104.7)	(23.7)	(43.7)
% Con. (Avg.)	(74.6)	(63.8)	(52.0)